Physicochemical studies on poly (vinyl alcohol) hydrogels(Dissertation_全文)

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PHYSICOCHEMICAL STUDIES ON POLY(VINYL ALCOHOL) HYDROGELS

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GENERAL INTRODUCTION

Hydrogels have been well known in foods such as "tokoroten" and jelly for a very long time. With the development of poly(2–hydroxyethyl methacryrate)(PHEMA) by Wichterle and Lim, hydrogel has come to knowledge in the polymer science[1] and the PHEMA hydrogel has been used widely as soft contact lens material[2]. A highly water–absorbable resin was developed by Fanta based on the hydrolysis of acrylonitrile grafted starch[3,4] and has grown to one of polymer industries at present. Furthermore, gels have attracted much attention as industrial materials since gel spinning was reported by Smith and Lemstra and high strength and high modulus fiber was produced from high molecular weight polyethylene[5,6].

On the other hand, 60–80% of living body consists of water. In other words, living body is composed of soft hydrogels except for hard tissues such as bone, tooth, nail, and hair. Therefore, hydrogel has been studied as biomaterial[7–13], but very few hydrogels have been used as biomaterial because synthetic hydrogels are much inferior to living body in mechanical properties and cannot insure long–term durability.

Polymeric hydrogel is composed of three–dimensional network from polymer chains which are insoluble in any solvent. There are basically two types of method for gel preparation[14,15]. One is the chemical crosslinking method and the other is the physical crosslinking. In the former case, functional groups on polymer chains are bound with crosslinking agent or radiation to form insoluble gels. On the other hand, the latter physical method introduces physical crosslinks between

polymer chains through intermolecular force. De Gennes has proposed the following three types as the structure formed by intermolecular force[15]; 1) helical structure from plural polymer chains, 2) crystallite, and 3) nodule from block copolymer. The gel formation from 1) has been found mostly in natural polymers such as protein and polysaccharide, whereas gel formation from the intermolecular force of 2) has been applied to the synthetic polymers, for example, poly(vinyl alcohol)(PVA)[16], polyethylene[17], polypropylene[18], polylactide[19], nylon 6[20], and ethylene–vinyl alcohol copolymer[20]. PVA is a hydrophilic crystalline polymer which has hydroxyl groups. It is predicted that high ultimate strength and modulus fiber will be produced from PVA, because PVA has planer zig–zag structure similar to polyethylene. The viscosity of aqueous PVA solution is known to increase, gradually setting to a gel through hydrogen bonding among the PVA segments when left standing at room temperature. Furthermore, specially treated PVA exhibits low protein adsorption[21] and low cell adhesion[22] and hence very inert to living body. Accordingly, if one can develop a PVA hydrogel having various properties such as high mechanical strength, transparency, and stickiness, it may become useful also as biomaterial, in addition to industrial material.

Gelation of PVA solution has been studied by many research groups and various methods have been proposed for PVA gelation[23–36]. Recently, physical crosslinking methods without any use of chemical crosslinking agent have attracted much attention because they allow us to prepare high strength and high water content PVA hydrogels[32–36]. This thesis is concerned with formation of PVA hydrogels by physical crosslinking without any crosslinking agent and their physicochemical

properties.

Chapter 1 describes preparation of PVA hydrogels by low temperature crystallization of aqueous PVA solution. The hydrogel structure is examined using wide–angle X–ray diffraction and the volume change of PVA hydrogel is measured with dilatometry. The hydrogel surface is viewed by scanning electron microscopy after critical–point drying of the hydrated gel. The tensile properties of PVA hydrogel is evaluated under the conventional conditions.

In Chapter 2, PVA hydrogel is prepared by low temperature crystallization of PVA solution in mixed solvents consisting of water and a water–miscible organic solvent. The dependence of mechanical properties of PVA hydrogel on gelation is studied for the solvent prepared from a mixture of water and a water–miscible organic solvent. The viscosity of concentrated PVA solution in mixed solvents is measured and the gelation time is determined using a small glass bar put in test tube containing PVA solution. The gelation temperature is determined by cooling the test tube containing the PVA solution. Light transmittance as well as tensile properties of PVA hydrogel are measured and the surface of PVA hydrogel is observed by scanning electron microscopy after critical–point drying.

Chapter 3 aims to study the transparent PVA hydrogels with various water contents prepared by annealing dried PVA hydrogels. The tensile strength and dynamic modulus of the hydrogels are measured with a tensile tester and a dynamic viscoelastometer, respectively. Testing is done over a temperature range from 25 to 100°C. The hardness and wear factor of PVA hydrogels are measured by a hardness tester and a "pin on disc" device, respectively. The crystallinity

of dried PVA hydrogels is estimated from the thermogram area of differential scanning calorimetry.

In Chapter 4, low temperature gelation of PVA solution is performed in the presence of $CaCl_2$ to obtain a sticky hydrogel. The water-holding ability of the PVA hydrogel is estimated from the weight change occurring when left at 25°C and a relative humidity of 65% while the degree of swelling of PVA hydrogel is determined by weighing the PVA hydrogel before and after immersion in water. The melting temperature of PVA hydrogel is measured by the Ferry method. The tensile properties as well as the peel strength of the sticky PVA hydrogel on a stainless steel are measured with the 90° peel strength method.

Chapter 5 is concerned with the microstructure of PVA hydrogels predicted from the state of water in hydrogel. The state of water in PVA hydrogels prepared from a mixture of water/dimethyl sulfoxide (DMSO) (20/80, w/w) by low temperature crystallization is investigated using differential scanning calorimetry over a wide range of water content. Sample is sealed between two pans using a pan crimper. After cooling to −80°C with liquid nitrogen, the hydrogel sample is heated at a rate of 10 °C/min in He. The heat of fusion is calculated from the thermogram area.

Chapter 6 deals with adsorption of protein on PVA hydrogels prepared by low temperature crystallization. Proteins used include γ-globulin, bovine serum albumin, and lysozyme. The proteins are labeled by ^{125}I using the Chroramine-T method. The adsorption experiment is carried out in labeled protein solution and the amount of adsorbed proteins is estimated from the radioactivity using a gamma-ray

scintillation counter.

Chapter 7 investigates the transparent PVA hydrogel which has a potentiality as soft contact lens material. To obtain hydrogel for soft contact lens, PVA solution is poured into a mold and allowed to stand in a refrigerator. The resulting PVA gel lens is removed from the mold and the organic solvent in gel lens is exchanged with water by immersing the gel in water. The PVA hydrogel contact lens is applied to albino rabbit eyes continuously for a period of 3 months. The central cornea thickness is measured using an ultrasonic pachymeter. The histological evaluation is attempted by light microscopy and scanning electron microscopy. The sample for light microscopy is prepared by staining with hematoxylin and eosin while the sample for scanning electron microscopy by the standard technique.

Chapter 8 reports PVA gel spinning from the PVA solution which has produced a dry gel film with the highest drawability. Gel spinning is performed by extruding spinning dopes with various PVA concentrations from a nozzle having a hole size of 0.6mm and the spinning dope is coagulated at various temperatures. Fiber drawing is attempted in a silicone oil bath kept at various temperatures and the tensile properties of drawn fiber are measured. Further, the melting temperature and heat of fusion of fiber are measured by differential scanning calorimetry. The crystallinity of PVA fiber is calculated from the thermogram area and the fiber density is measured with the density gradient method using mixtures of benzene and carbon tetrachloride. The X-ray diffraction pattern of fiber is taken with a flat camera and the surface of PVA fiber is observed with scanning electron microscopy.

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CHAPTER 1

Formation of poly(vinyl alcohol) hydrogel by low temperature crystallization of aqueous poly(vinyl alcohol) solutions

INTRODUCTION

An aqueous PVA solution gradually sets to a gel through hydrogen bonding among the PVA segments when left standing at room temperature, but this hydrogel is poor in mechanical properties[1-3]. To obtain higher strength PVA hydrogels, covalent crosslinking has been attempted using chemical agents and radiation[4-6]. Although these methods yield PVA hydrogels with high strength, their water content is low. On the other hand, physical crosslinking without any use of chemical agents has been studied by several research groups[7-10]. One method is freezing of highly concentrated aqueous PVA solution[7]. The PVA hydrogel obtained is insufficient in mechanical properties and, in addition, swellable in water. Therefore, partial freeze-drying of aqueous PVA solution under vacuum[8] and repeating of freezing and thawing cycle of concentrated aqueous PVA solution[9,10] were attempted by Watase et al. PVA hydrogels prepared by these methods have high water content, high strength, and rubber-like elasticity. It is thought that such PVA hydrogels are formed as a result of crystallization of PVA molecules. Thus the crystallization condition of PVA molecular chain in aqueous solution is very important in order to obtain high strength and high water content gels. This Chapter describes the preparation of PVA hydrogel by standing frozen concentrated aqueous PVA solutions at low

temperature to proceed crystallization of PVA molecular chains.

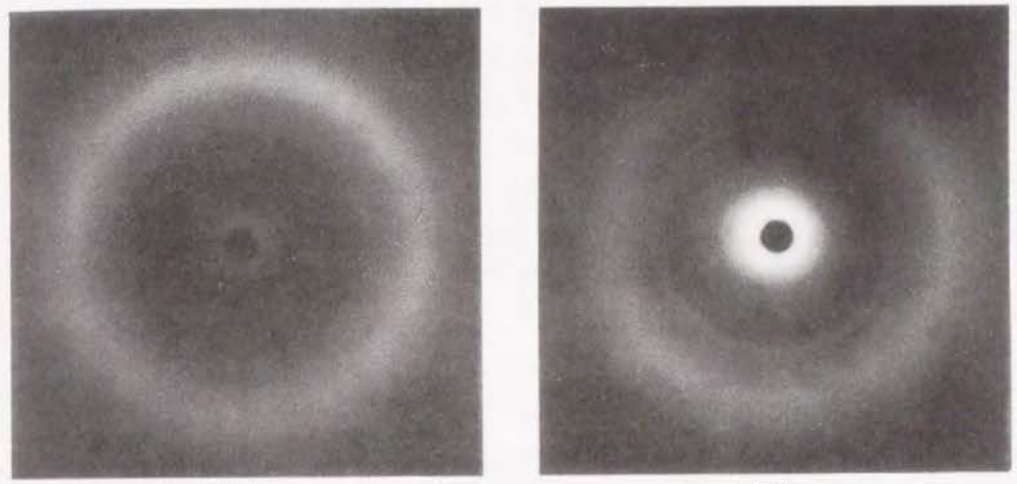
EXPERIMENTAL

1. Gel formation

PVA used has a viscosity-average degree of polymerization of 1,700 and a degree of saponification of 99.5 mol%. An aqueous PVA solution with the polymer concentration range from 10 to 30 wt% was prepared at 110°C using an autoclave. After the temperature of solution was lowered to 60°C, it was cast on a glass plate, followed by freezing at -20°C. This frozen PVA solution was thawed under three different conditions; 1) in the flowing water at 18°C for 10 min, 2) at 20°C for 3 hr, and 3) at 5°C for 10 hr.

2. Physical measurements

Wide-angle X-ray diffraction patterns of PVA hydrogels were obtained with a flat camera using Ni-filtered Cu-Kα and an X-ray diffraction apparatus Ru-3 of Rigakudenki Co.Ltd.,Tokyo, Japan and the diffraction profiles were measured with a scintillation counter. The volume change of PVA hydrogel at 5 and 20°C up to 72 hr was measured by dilatometry. A gel sample was melted in dilatometry at 100°C, followed by freezing at -20°C for 24 hr. The degree of swelling and shrinkage of PVA hydrogel was determined by weighing the PVA hydrogel before and after immersion in water at 37°C. ^{13}C-NMR spectra of PVA hydrogel were obtained at 50 MHz using a JOEL GX-400 spectrometer of Japan Electronic Co.Ltd.,Tokyo, Japan. Tensile strength and elongation were measured with a tensile tester at 25°C under a



(A) (B)

Figure 1. Wide-angle X-ray diffraction patterns of PVA hydrogels with 10 and 20 wt% PVA concentrations. (A) 10 wt% ; (B) 20 wt%

tensile speed of 50 mm/min using Autograph S-100 of Shimadzu Inc., Kyoto, Japan. A hydrogel sample was cut to dumb-bell test pieces in accordance with JIS specifications. The hydrogel surface was observed by scanning electron microscopy(SEM) using a Hitachi S-450 SEM apparatus after critical-point drying of the hydrated gel using 3-methylbutyl acetate.

RESULTS

1. X-ray diffraction

Figure 1 shows wide-angle X-ray diffraction patterns of PVA hydrogels prepared by freezing 10 and 20 wt% PVA solutions at -20°C

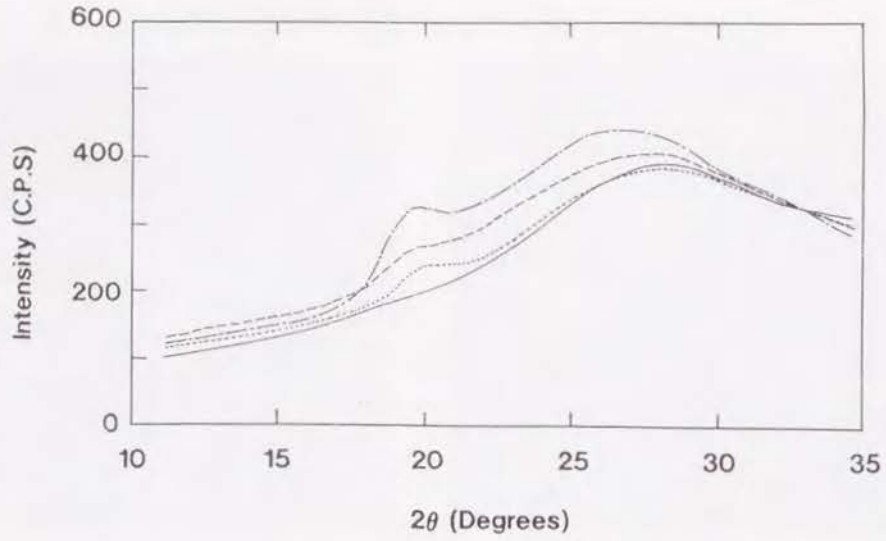


Figure 2. Wide-angle X-ray diffraction profiles of PVA hydrogels. (—) thawing in flowing water at 18°C for 10 min, 20 wt% (·····) thawing at 5°C for 10 hr, 10 wt% ; (- - -) thawing at 5°C for 10 hr, 20 wt% ; (-·-) thawing at 5°C for 10 hr, 30 wt%

for 24 hr, followed by thawing at 5°C for 10 hr. The X-ray diffraction patterns of PVA hydrogel prepared by rapid thawing in the flowing water at 18°C for 10 min displayed only amorphous halo containing also the scattering from water. In contrast, as shown in Figure 1, the PVA hydrogel prepared by slow thawing at lower temperature(5°C) has a diffraction pattern of crystallite in the small angle side. This tendency is seen more clearly for the 20 wt% PVA hydrogel.

Figure 2 represents wide-angle X-ray diffraction profiles of PVA hydrogels prepared under various thawing conditions. The 20 wt% PVA hydrogel prepared by rapid thawing in flowing water at 18°C for 10 min has only one broad peak around $2\theta=27°$, whereas the 20 wt% PVA hydrogel prepared by slow thawing at 5°C for 10 hr shows a new peak

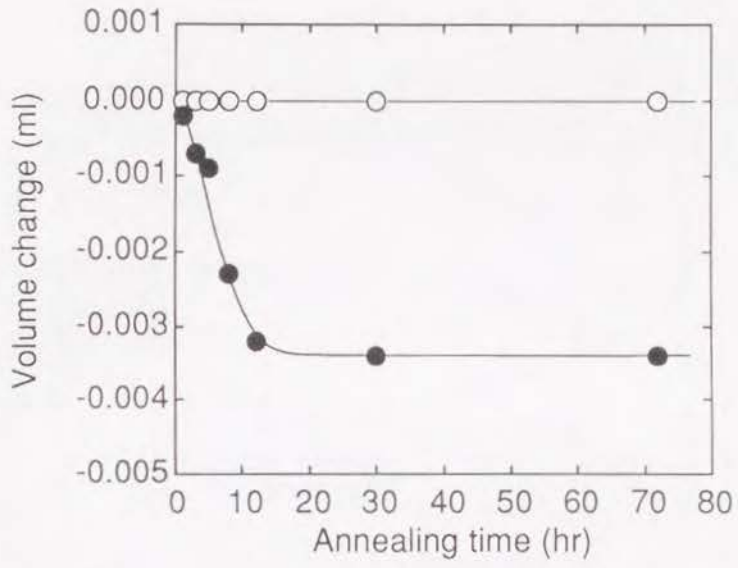


Figure 3. Volume change of 20 wt% hydrogel at 5 and 20°C with time. (●) 5°C ; (○) 20°C

around 19.5°, which increases with increasing PVA concentration. This peak corresponds to the (101) reflection of crystal structure of PVA. This result indicates that PVA in solution is crystallized during slow thawing at 5°C. Therefore, we call the crystallization of PVA by slow thawing at 5°C the low temperature crystallization.

2. Dilatometry

The volume change of PVA hydrogel occurred which has at 5 and 20°C is shown as a function of time in Figure 3. At 20°C, the PVA hydrogel volume remains almost unvaried with elapse of time. On the other hand, the PVA hydrogel volume gradually decreases at 5°C up to 10 hr and subsequently levels off, but the volume decrease is so small as 0.035. The result of wide-angle X-ray diffraction suggests that this volume change is induced by crystallization of PVA chains.

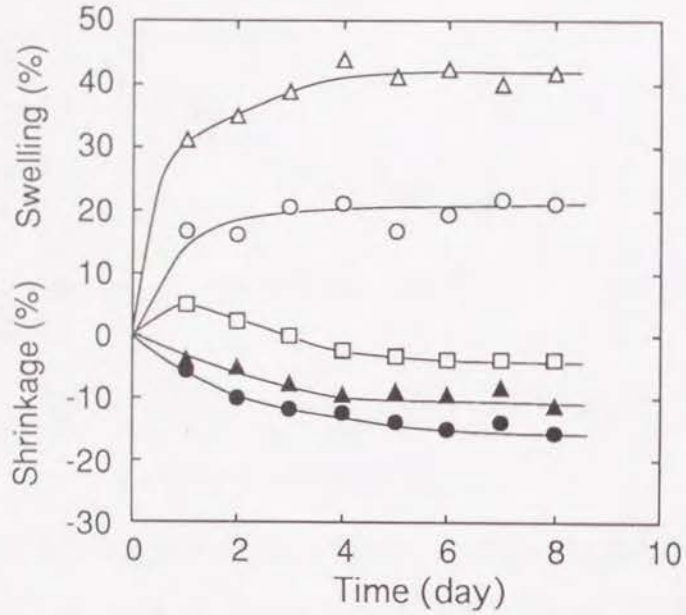


Figure 4. Swelling and shrinkage of PVA hydrogels in water at 37°C.
(○) thawing in flowing water at 18°C for 10 min, 10 wt%
(△) thawing in flowing water at 18°C for 10 min, 20 wt%
(●) thawing at 5°C for 10 hr, 10 wt%
(▲) thawing at 5°C for 10 hr, 20 wt%
(□) thawing at 20°C for 3 hr, 10 wt%

3. Swelling and shrinkage

The swelling and shrinkage of PVA hydrogels prepared under various conditions in water are shown in Figure 4 as a function of time. As is seen, it depends on the preparation conditions. The degree of swelling of 10 and 20 wt% PVA hydrogels prepared by rapid thawing in flowing water at 18°C for 10 min increases with time and approaches a constant value after 4 day. Furthermore, the degree of swelling of PVA hydrogel is higher as the PVA concentration of PVA solution is higher.

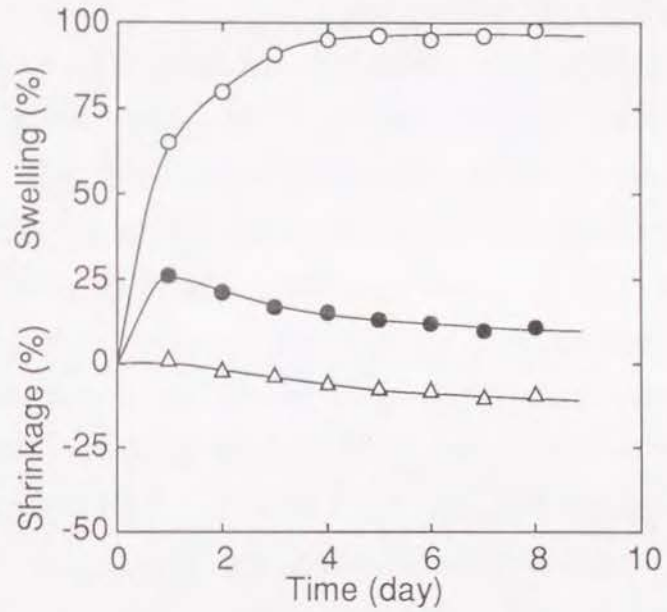


Figure 5. Swelling and shrinkage of 15 wt% PVA hydrogels in water at 37°C.
Freezing time : (○) 2 hr ; (●) 5 hr ; (△) 12 hr

The PVA hydrogel prepared by thawing at 20°C for 3 hr reaches a maximum at 1 day and then gradually decreases. In contrast, the PVA hydrogel prepared by low temperature crystallization at 5 °C gradually shrinks up to 4 day but the shrinkage subsequently stops. In addition, the degree of shrinkage of PVA hydrogel depends on the PVA concentration. 10 wt% PVA hydrogel exhibits higher shrinkage than 20 wt% PVA hydrogel. The swelling of the PVA hydrogel prepared by rapid thawing in flowing water at 18°C for 10 min may vary as a result of partial dissolution of microcrystallites due to its unstable gel structure. In contrast, the PVA hydrogel prepared by low temperature

crystallization undergoes shrinkage due to further crystallization of the amorphous part of PVA with aging.

Figure 5 shows the swelling and shrinkage of 15 wt% PVA hydrogel as a function of freezing time. The PVA solution was frozen at −20°C for different periods of time and crystallized at 5°C for 10hr. The degree of swelling of the PVA hydrogel strongly depends on the freezing time. The PVA hydrogel frozen for 2 hr swells with time, suggesting formation of an unstable gel. The PVA hydrogel frozen for 5 hr indicates maximum swelling after 1 day and subsequently deswells with time. On the other hand, the PVA hydrogel frozen for 12 hr shrinks with time to indicate that this has a relatively high strength. This result denotes that, similar to the thawing, the freezing condition is very important to obtain a high water content and high strength PVA hydrogel.

4. NMR spectra

Figure 6 represents ^{13}C NMR spectra of PVA hydrogels prepared with different methods. The PVA hydrogels prepared by aging from standing at room temperature and those by chemical crosslinking using glutaraldehyde were both transparent, whereas the PVA hydrogel prepared by low temperature crystallization was translucent. Furthermore, the mechanical properties depended on the preparation method. The highest strength was obtained by preparing the PVA hydrogel through low temperature crystallization, but as shown in Figure 6, the spectra of each PVA hydrogel show no difference among the preparation methods, although the transparency and mechanical properties of hydrogels are greatly different.

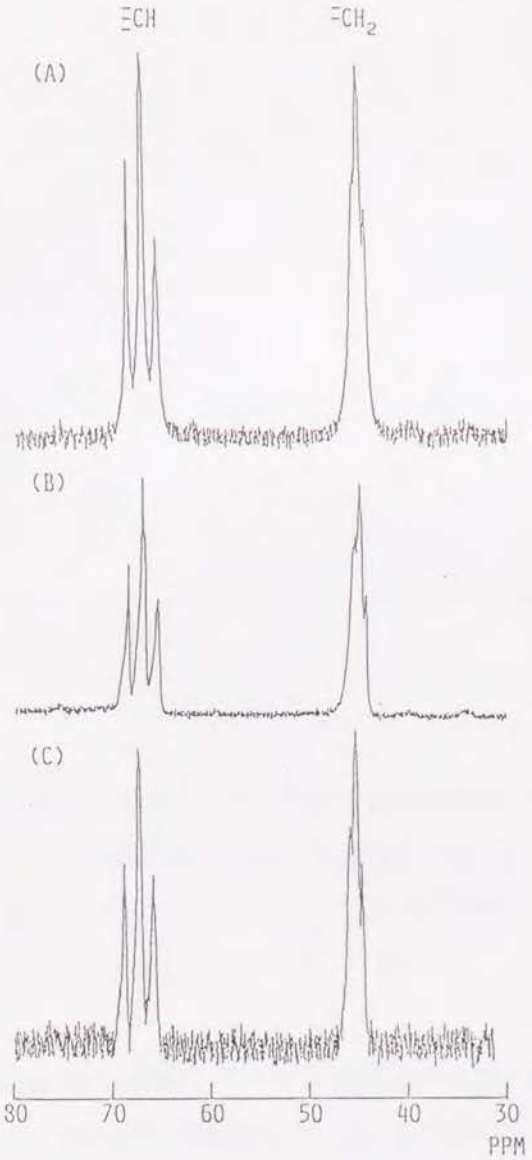


Figure 6. ^{13}C NMR spectra of PVA hydrogels.
(A) low temperature crystallized gel, 20 wt%
(B) aging gel from standing at room temperature, 20 wt%
(C) crosslinked gel with glutaraldehyde, 20 wt%

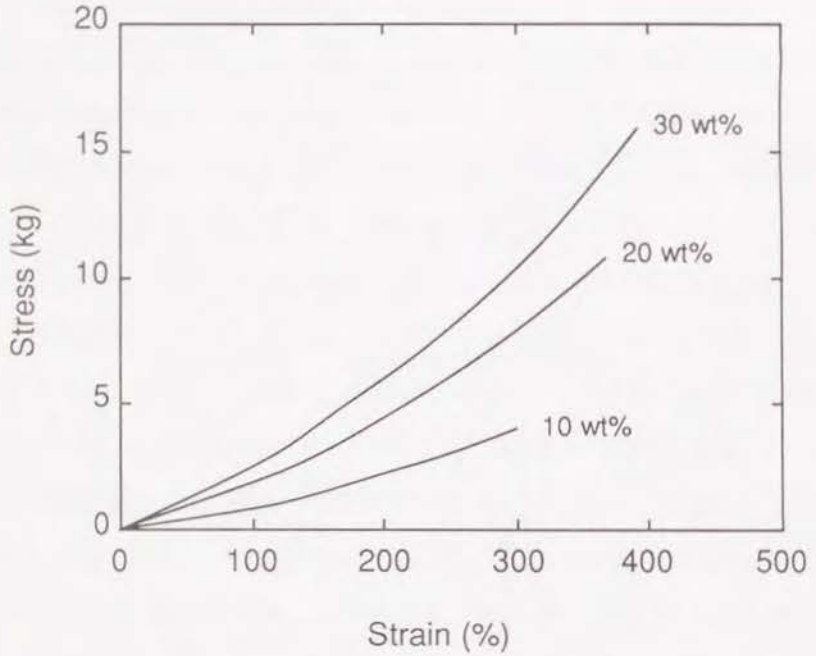


Figure 7. Stress–strain curves of PVA hydrogels prepared by low temperature crystallization at different PVA concentrations.

5. Tensile properties

Stress–strain curves of PVA hydrogels prepared by low temperature crystallization are shown in Figure 7. Apparently, the stress–strain curves differ from those of plastic, fiber, and elastomers but are similar to that of living organisms[11]. The tensile strength and elongation of the PVA hydrogels are shown in Figures 8 and 9. The PVA hydrogel prepared by rapid thawing in flowing water at 18°C for 10 min could not give a measurable value because of too weak mechanical properties. As can be seen from Figures 8 and 9, the tensile

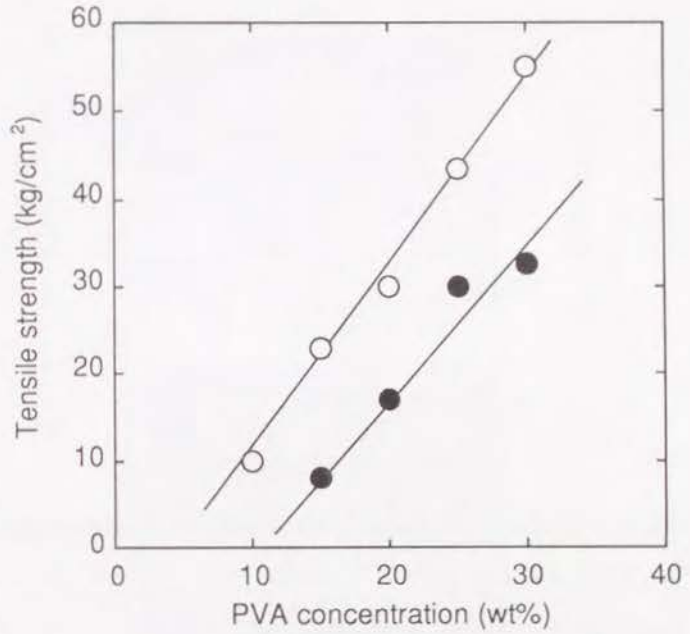


Figure 8 . Tensile strength of PVA hydrogels prepared at different PVA concentrations.
(●) slowly melted at 20°C for 3 hr
(○) crystallized at 5°C for 10 hr

strength and elongation of PVA hydrogel strongly depend on the PVA concentration and crystallization conditions. Low temperature crystallization gives the highest mechanical values for PVA hydrogels. In general, as the crosslinking density increases, the strength of hydrogel increases but elongation decreases. However, as shown in Figures 7, 8, and 9, the tensile strength and elongation of PVA hydrogel prepared by low temperature crystallization increase with the increasing PVA concentration in the concentration range studied.

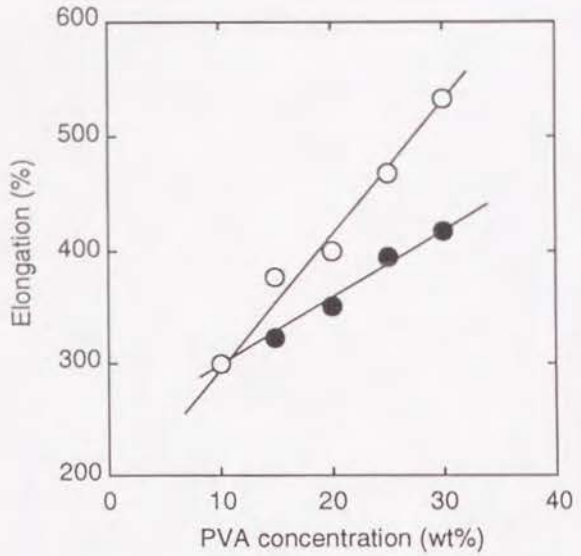


Figure 9. Tensile elongation of PVA hydrogels prepared at different PVA concentrations.
(●) slowly melted at 20°C for 3hr
(○) crystallized at 5°C for 10 hr

6. SEM observation

The structure of PVA hydrogel is partially destroyed accompanying shrinkage, when it is subjected to freeze-drying. Consequently, its sample for SEM observation should be prepared by critical-point drying to view the PVA hydrogel surface similar to the SEM sample of living organisms. The SEM photographs of PVA hydrogels prepared by low temperature crystallization are given in Figure 10. Obviously, the PVA hydrogel surface has porous structure and the pore size is smaller for more highly concentrated PVA hydrogel. For example, the pore size of 10 wt% PVA hydrogel is 5μm, whereas that of 30 wt% PVA hydrogel is less than 1μm.

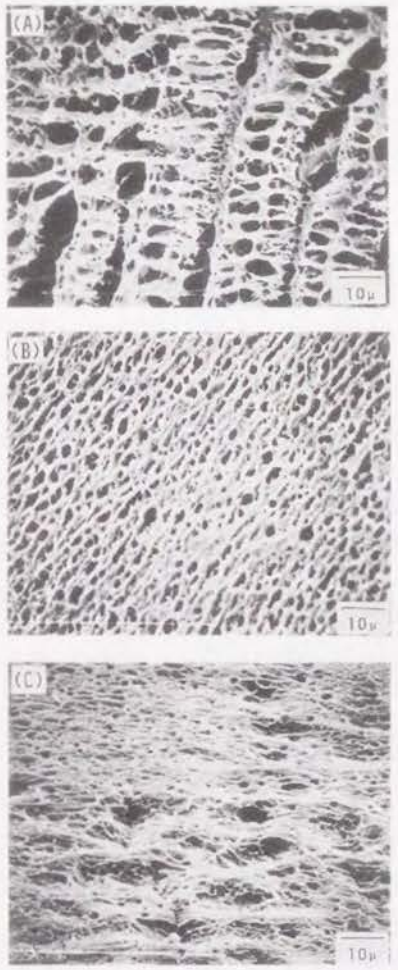


Figure 10. SEM photographs of PVA hydrogels prepared by low temperature crystallization at different PVA concentrations.
(A) 10 wt% ; (B) 20 wt% ; (C) 30 wt%

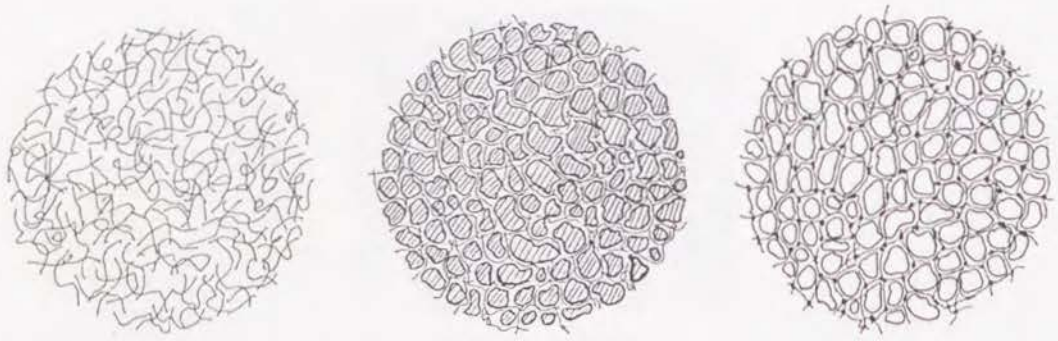


Figure 11. Schematic representation of gel formation.
(A) concentrated aqueous PVA solution before freezing
(B) frozen PVA solution before crystallization with ice
(C) gel simultaneously melted and crystallized

DISCUSSION

As is known, concentrated aqueous PVA solutions set to a gel when aged, but do not yield high water content and high strength PVA hydrogels. As described above, high water content and high strength PVA hydrogels can be obtained by freezing a concentrated aqueous PVA solution and subsequent slow crystallization at low temperature. The most important factor found in this study to obtain high strength and high water content PVA hydrogels is the conditions for PVA crystallization as well as for freezing the concentrated aqueous PVA solution. The scheme of PVA hydrogel formation is illustrated in Figure

11. PVA solution is homogeneous at high temperatures as shown in Figure 11 (A). When the homogeneous PVA solution is frozen, PVA chains are excluded from the ice, resulting in phase separation into a PVA-poor and a PVA-rich phase as is seen in Figure 11 (B). Microcrystallites of PVA are formed in the PVA-rich phase when allowed to stand at low temperature for long time because the PVA concentration increases in a local area and simultaneously PVA crystallization proceeds in the course of thawing. The resulting microcrystallites act as strong crosslinks of three-dimensional network structure in the PVA-rich phase and then the water is packed in the gap between networks, leading to formation of porous structure such as shown in Figure 11 (C). Consequently, the PVA hydrogel prepared by low temperature crystallization must have high water content, high strength, and microporous structure.

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CHAPTER 2

Preparation of transparent poly(vinyl alcohol) hydrogels with high water contents

INTRODUCTION

In Chapter 1, it was reported that the high water content and high strength PVA hydrogel was prepared by low temperature crystallization of concentrated aqueous PVA solutions. These PVA hydrogels have high water content, high strength, and rubber-like elasticity, but are optically translucent.

This Chapter deals with the preparation of a transparent PVA hydrogel with high water content and high strength. As described in Chapter 1, when a concentrated aqueous PVA solution is frozen, phase separation into a PVA-poor and a PVA-rich phase may take place, resulting in PVA crystallization in the phase-separated state to give a translucent PVA hydrogel with porous structure. If this mechanism is correct, it seems likely that a transparent PVA hydrogel will be obtained by low temperature crystallization of PVA at the non-frozen state of PVA solution, in other words, under the condition where phase separation does not take place. To confirm this assumption, this Chapter is studied crystallization of PVA solutions at low temperature in mixed solvents consisting of water and a water-miscible organic solvent to avoid macroscopic phase separation.

EXPERIMENTAL

1. Preparation of PVA hydrogel

The PVA used has a viscosity-average degree of polymerization (DP) of 1,000, 1,700, 3,200, and 4,800 with a degree of saponification of 99.5 mol%. Unless otherwise specified, PVA with DP of 1,700 was used throughout this work. The organic solvents to be mixed with water include glycerin(GC), ethylene glycol(EG), dimethyl sulfoxide (DMSO), and 1,3,-dimethyl-2-imidazolidinone(DMI). All the chemicals were used as obtained. Homogeneous PVA solutions with concentrations ranging from 5 to 25 wt% were prepared by heating the mixture of PVA powder, water, and an organic solvent at 140°C for 2 hr in N_2 atmosphere. When the temperature of PVA solution was lowered to 60°C, the solution was cast on a glass plate and allowed to stand for PVA crystallization at various temperatures. The gel obtained as a result of PVA crystallization was placed in flowing water for 4 days to exchange the organic solvent in the gel with water.

2. Physical measurements

Viscosities of concentrated PVA solution in mixed solvents were measured at 60°C using a rotation viscosity meter(Yagami Emila Rheometer). Gelation time was determined as the time when a small glass bar put in a 30mm test tube containing 25ml of the PVA solution could not move any more upon tilting the tube placed in a −10°C methyl alcohol bath. Also, gelation temperature was determined by cooling the test tube containing the PVA solution at a rate of 2 °C/min in the methyl alcohol bath, while melting temperature was estimated by heating the

test tube containing the PVA gel at a rate of 2 °C/min. In both the cases, movement of the glass bar placed in the PVA solution or gel was observed with naked eye to determine the respective characteristic temperatures.

Light transmittance of PVA hydrogels was measured at 25°C with a spectrophotometer at 570nm for hydrogels of 0.6 or 1.5mm thickness. Tensile properties of PVA hydrogels were measured with a tensile tester at a cross-head speed of 50 mm/min at 25°C and relative humidity of 65%. The membrane samples were cut to dumb-bell test pieces in accordance with JIS specifications. All these measurements were done on the PVA hydrogels in the hydrated state.

The hydrogel surface was observed by scanning electron microscopy(SEM) using Hitachi S-450 after critical-point drying of the hydrated gel using 3-methylbutyl acetate.

The phase transition of water/DMSO mixed solvent was studied using DSC. NMR spectra of PVA solution were obtained at 50°C with a Varian VXR300 spectrometer.

RESULTS

1. Gelation of PVA solution

Figure 1 shows the viscosity of 10 wt% PVA solutions in mixed solvents of different compositions at 60°C. It is apparent that the solution viscosity depends not only on the mixing ratio of water and the organic solvent but also on the nature of the organic solvents used. The PVA solution prepared from mixtures of water/GC and water/EG exhibits a continuous increase in viscosity with the increasing

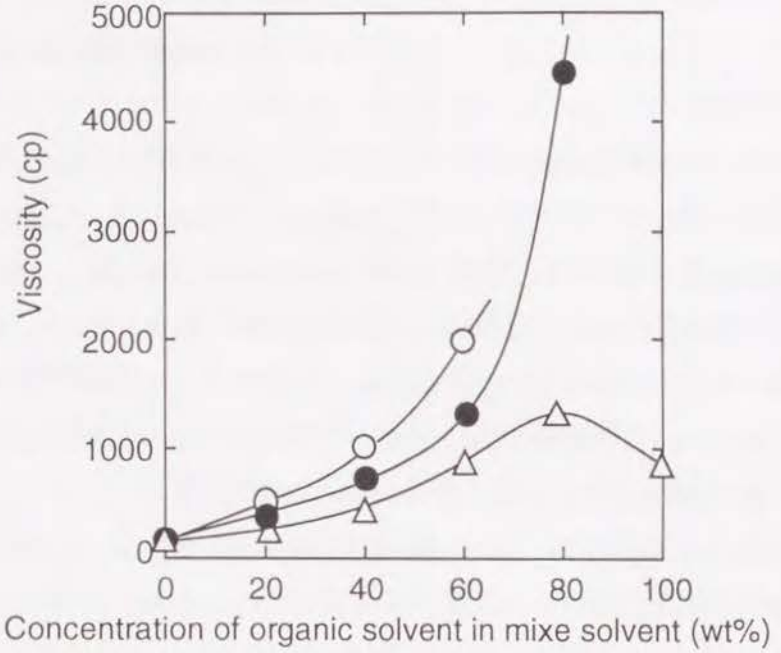

Figure 1. Effect of the concentration of organic solvent in mixed solvents on the viscosity of 10 wt% PVA solution at 60°C.
(○) GC ; (●) EG ; (△) DMSO

concentration of GC and EG in the mixed solvents. When 100 wt% GC or EG was used as solvent, the viscosity could not be measured because gelation occurred at 60°C. The mixed solvents from water/DMSO give the composition dependence of solution viscosity clearly different from that of water/GC and water/EG. The viscosity of solution prepared from mixtures of water/DMSO increases as the DMSO concentration approaches 80 wt% but decreases at higher DMSO concentrations. The mixed solvent from water/DMI indicated the same tendency on the solution viscosity as that of water/GC and water/EG.

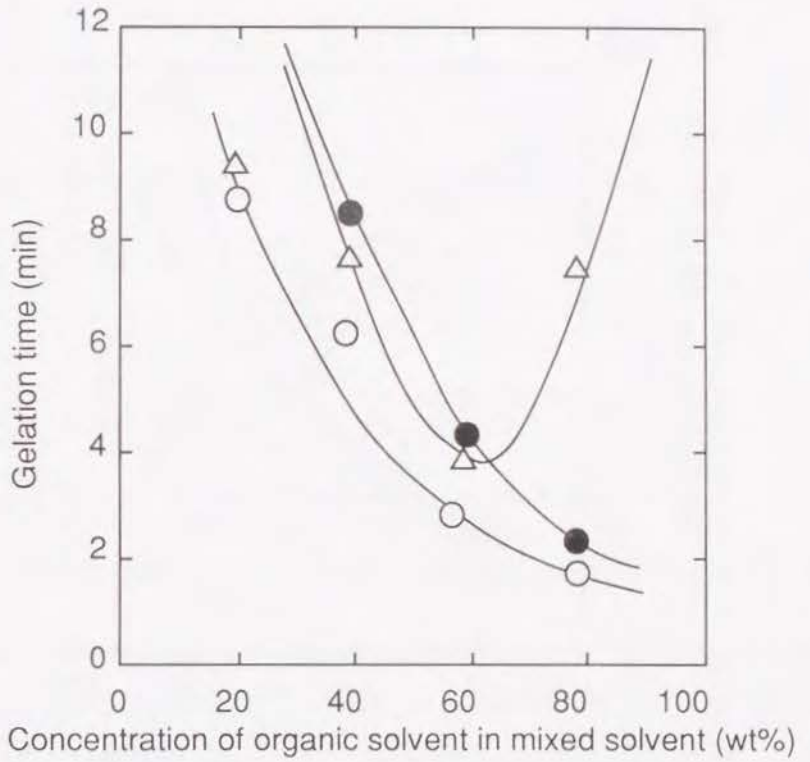

Figure 2. Effect of the concentration of organic solvent in mixed solvents on the gelation time on 5 wt% PVA solution at −10°C.
(○) GC ; (●) EG ; (△) DMSO

The incipient gelation time of 5 wt% PVA solution at −10°C is given in Figure 2. Comparison of Figure 2 with Figure 1 reveals that the gelation time has a strong correlation with the solution viscosity with respect to the composition dependence of mixed solvents. The gelation time is generally shorter for the PVA solution of higher viscosity. The solution obtained from mixtures of water/DMSO shows a minimum gelation time near 60 wt% DMSO concentration, lower than 80 wt% where the solution viscosity showed the maximum.

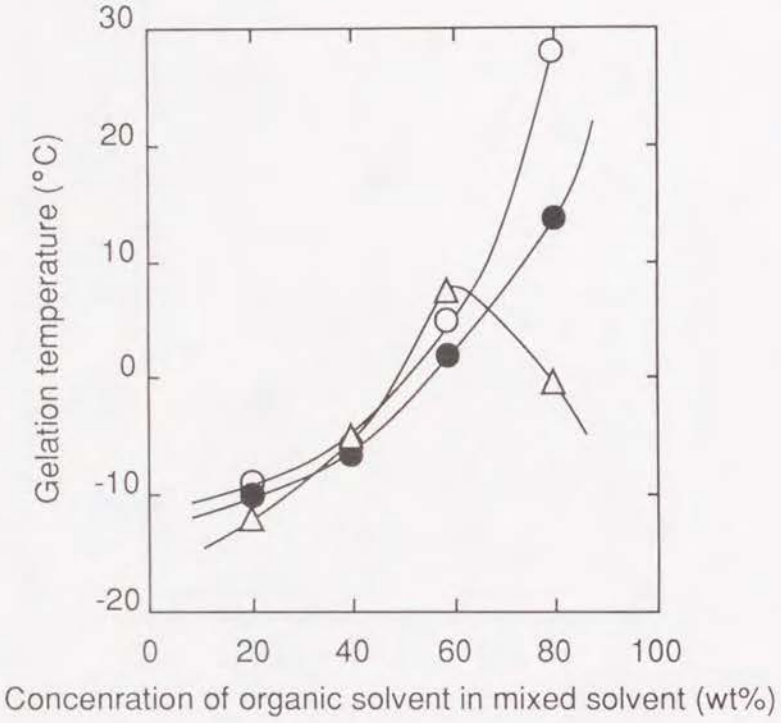

Figure 3. Effect of the concentration of organic solvent in mixed solvents on the gelation temperature of 5 wt% PVA solutions.
(○) GC ; (●) EG ; (△) DMSO

Figure 3 gives the incipient gelation temperature of 5 wt% PVA solution plotted as a function of the organic solvent concentration in the mixed solvents. The dependence of gelation temperature on the composition of mixed solvents is similar to that of gelation time. The gelation temperature of PVA solutions prepared from water/GC and water/EG mixtures is higher as the solution viscosity at 60°C is higher, while the solution from water/DMSO has the highest gelation temperature at 60 wt% DMSO concentration.

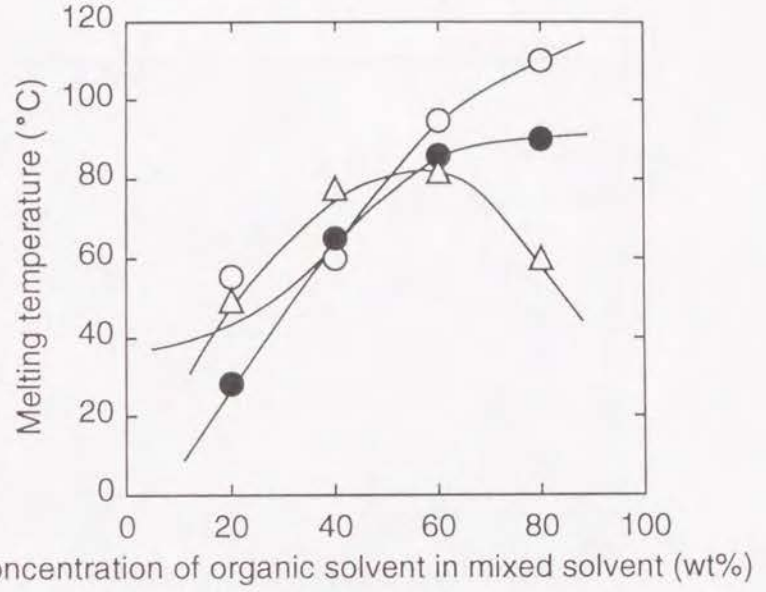

Figure 4. Effect of the concentration of organic solvent in mixed solvents on the melting temperature of the PVA gel crystallized from 5 wt% PVA solution at −20°C for 24 hr.
(○) GC ; (●) EG ; (△) DMSO

The variation in melting temperature of the PVA gel crystallized at −20°C with the concentration of organic solvent in the mixed solvents is given in Figure 4. The dependence of gel melting temperature on the solvent composition is quite similar to that of gelation temperature. A similar result was reported by Yamaura et al[1].

2. Transparency of PVA hydrogel

Figure 5 shows the light transmittance at 570nm for the PVA hydrogels prepared from 20 wt% solution of water/DMSO at −20°C. The PVA hydrogels had a thickness of 0.6mm. The PVA hydrogel prepared from 100 wt% water exhibited light transmittance of 40%, but

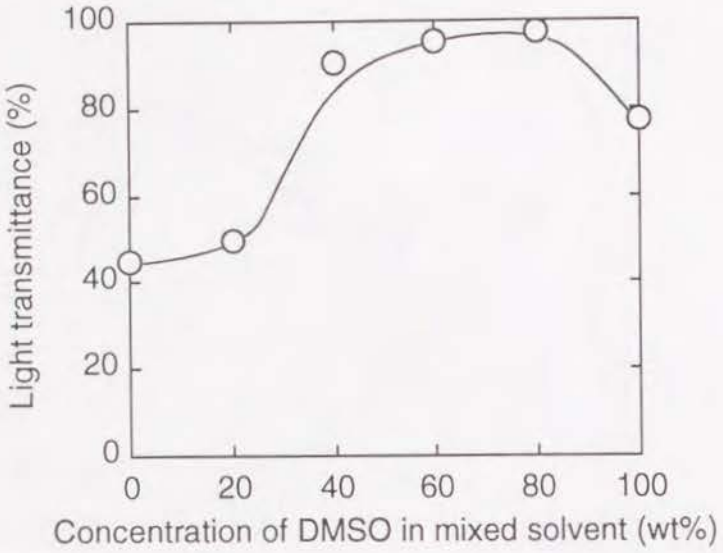

Figure 5. Effect of the DMSO concentration in solution on the light transmittance of the PVA hydrogel crystallized from 20 wt% PVA solution at −20°C for 24 hr.
(570nm, 0.6mm thickness)

it increased with the increasing DMSO concentration, approaching a maximum(99%) at 80 wt% DMSO concentration. The mixed solvents of water/GC, water/EG, and water/DMI gave light transmittance higher than 90% when the concentration of organic solvent ranged from 40 to 60 wt%, but substantially lower light transmittance than the water/DMSO mixtures. The light transmittance of hydrogel increased with the crystallization time. The result is given in Figure 6 for the PVA hydrogels obtained at various crystallization temperatures. The PVA hydrogel thickness was 1.5mm and the mixed solvent used was 80 wt% DMSO solution, which showed the highest transparency among the mixed solvents. As is seen in Figure 6, the hydrogel transmittance is

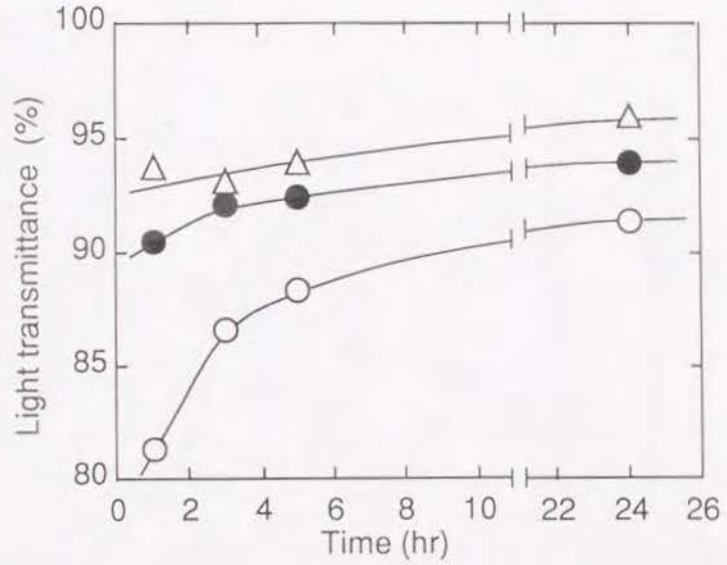

Figure 6. Effect of the crystallization time on the light transmittance of PVA hydrogel obtained from 20 wt% PVA solution in 80 wt% DMSO at different temperature.
(570nm, 1.5mm thickness)
(△) −20°C ; (●) 4°C ; (○) 25°C

higher for lower crystallization temperature. The dependence of the light transmittance on the crystallization time clearly differs from that of the crystallization temperature. When PVA solution was crystallized at 25°C, the light transmittance increased most steeply with the crystallization time but approached only 91% after 24 hr. In contrast, the light transmittance of the PVA hydrogel obtained at −20°C was higher than 90% after 1 hr and reached 96% after 24 hr.

3. Tensile properties of PVA hydrogel

Tensile strength and elongation of the PVA hydrogels prepared

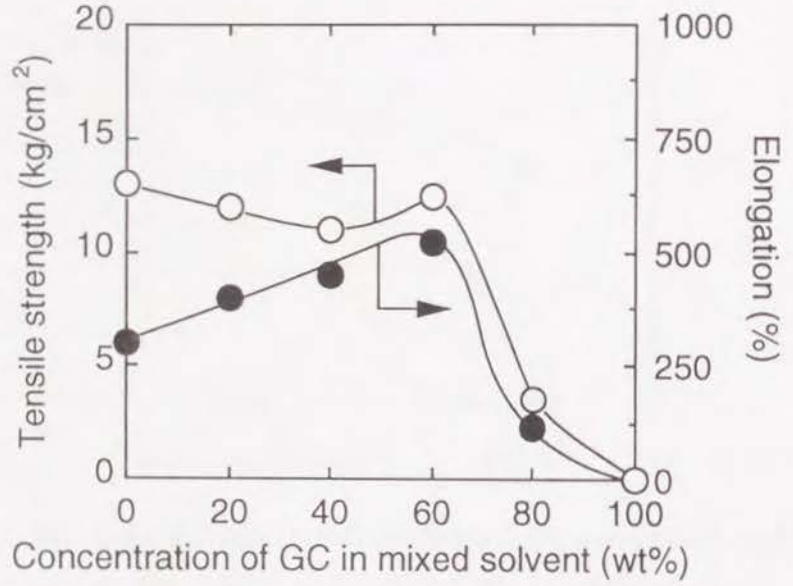

Figure 7. Tensile strength and elongation of the PVA hydrogel crystallized from 15 wt% PVA solution at −20°C for 24 hr as a function of GC concentration in mixed solvents.

from mixed solvents from water/GC at −20°C are shown in Figure 7. The tensile strength of PVA hydrogel prepared at the GC concentration below 60 wt% is almost equal to that of hydrogel prepared from 100 wt% water. However, the tensile strength, as well as the elongation, drastically decreased at GC concentrations higher than 60 wt%. 100 wt% GC solution also yielded a hydrogel, but its strength and elongation were almost zero. Figures 8 and 9 show the tensile strength and elongation of PVA hydrogels prepared at −20°C from water/DMI and water/DMSO, respectively. The tensile strength and the elongation are highly dependent on the concentration of organic solvent, giving a

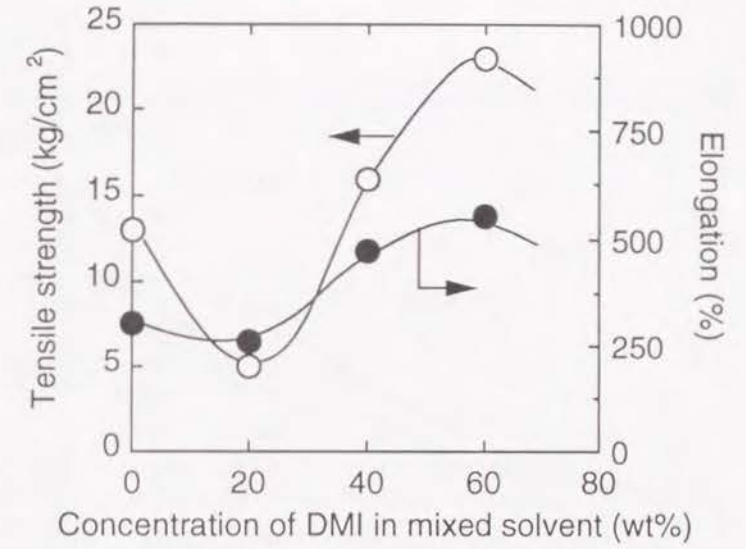

Figure 8. Tensile strength and elongation of the PVA hydrogel crystallized from 15 wt% PVA solution at −20°C for 24 hr as a function of DMI concentration in mixed solvent.

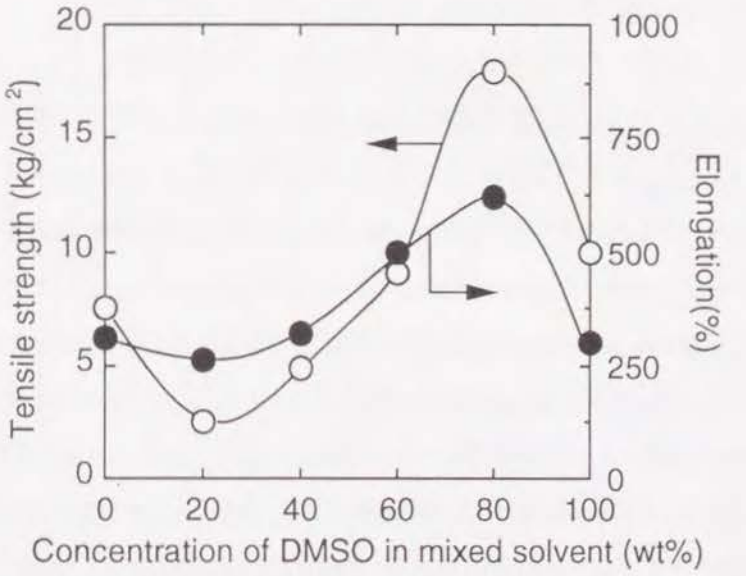

Figure 9. Tensile strength and elongation of the PVA hydrogel crystallized from 12 wt% PVA solution at −20°C for 24 hr as a function of DMSO concentration in mixed solvent.

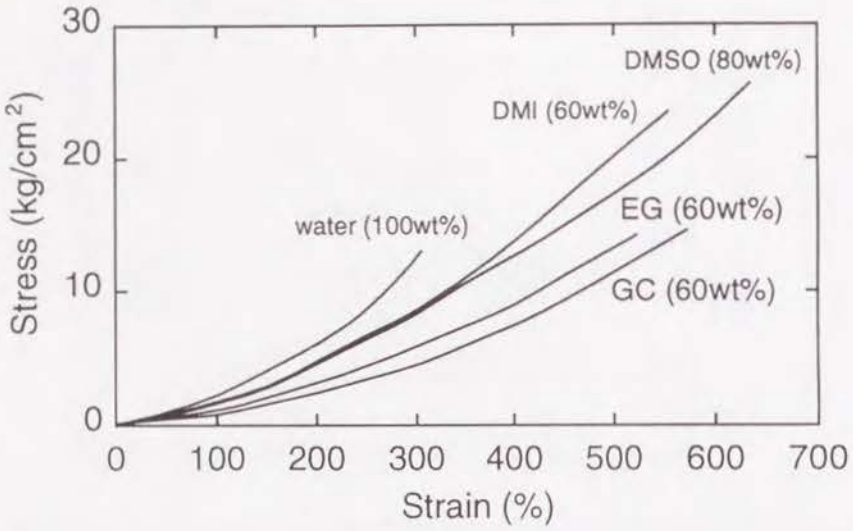

Figure 10. Stress–strain curves of the PVA hydrogels crystallized from 15 wt% PVA solution of different mixed solvents at –20°C for 24 hr.

maximum and a minimum for both the solvents. The difference in mechanical property between DMI and DMSO is not significant. The small difference may be partly due to the PVA concentration where the solution crystallization was effected.

The stress–strain curves of PVA hydrogels prepared under the condition yielding the maximum strength for each type of organic solvents are shown in Figure 10. The water content of PVA hydrogels is mostly 85 wt%. It is seen that the PVA hydrogels prepared from water/DMSO and water/DMI have better mechanical properties than those prepared using other solvents. Also, all of the PVA hydrogels prepared from mixtures of water and an organic solvent give a similar or higher strength than the PVA hydrogel prepared from 100 wt% water.

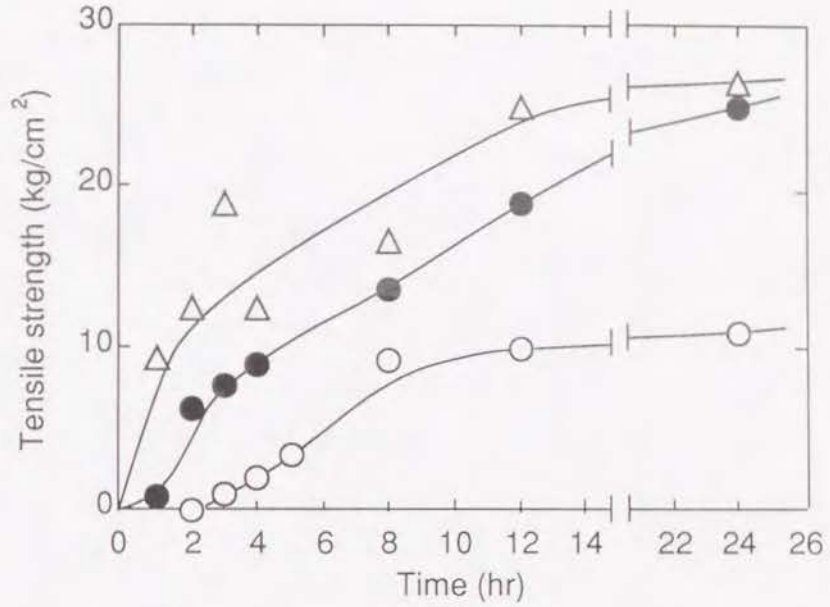

Figure 11. Effect of the standing time on the tensile strength of the PVA hydrogel crystallized from 15 wt% PVA solution in 80 wt% DMSO at different temperature.
(△) –20°C ; (●) 4°C ; (○) 25°C

The influence of crystallization temperature on the tensile strength of PVA hydrogel was investigated for the mixed solvent of 80 wt% DMSO, as it gave the highest tensile strength among the mixed solvents. The result is given in Figure 11. The tensile strength of PVA hydrogel clearly varies with the crystallization temperature. When crystallized at 25°C, PVA solution did not undergo gelation until to 2 hr and the tensile strength of gels resulting after that only slightly increased with time. On the other hand, the PVA hydrogel prepared at –20°C exhibited high tensile strength even after 1 hr and approached a strength 2.5 times as high as that prepared at 25°C after 24 hr.

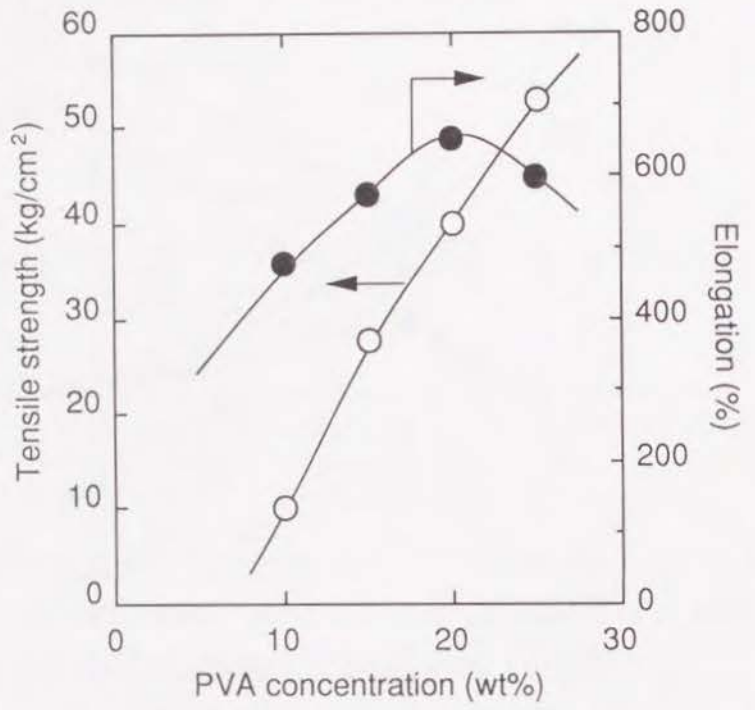

Figure 12. Effect of the PVA concentration on the tensile strength and elongation of PVA hydrogel crystallized from PVA solutions of different PVA concentration in 80 wt% DMSO at −20°C for 24 hr.

Figure 12 shows the dependence of tensile strength and elongation of PVA hydrogels crystallized at −20°C on the PVA concentration. The crystallization period was 24 hr. The tensile strength of PVA hydrogel increases with increasing the PVA concentration. On the other hand, the elongation of PVA hydrogel increases up to 20 wt% but decreases at higher PVA concentration. It seems that this result is due to the increasing of junction point for the crosslinking.

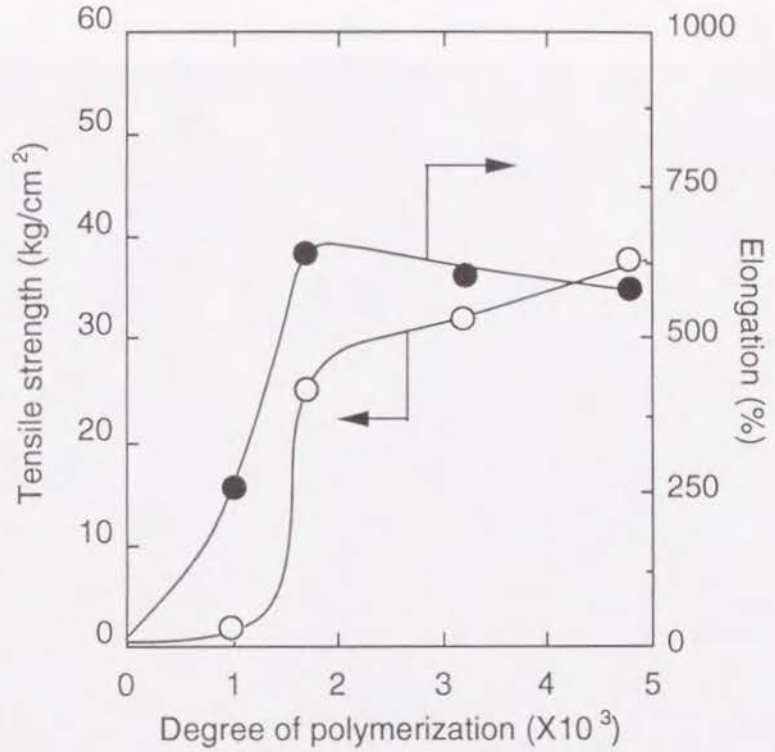

Figure 13. Effect of the degree of polymerization of PVA on the tensile strength and elongation of PVA hydrogel crystallized from 15 wt% PVA solution in 80 wt% DMSO at −20°C for 24 hr.

The tensile strength and elongation of PVA hydrogel as a function of degree of polymerization is given in Figure 13. At 1,000, the tensile strength of PVA hydrogel is very weak. The strength of PVA hydrogel increases drastically at 1,700 and afterward increases slightly with the increasing degree of polymerization. In contrast, the elongation of PVA hydrogel increases drastically up to 1,700 and subsequently decreases with the increasing degree of polymerization.

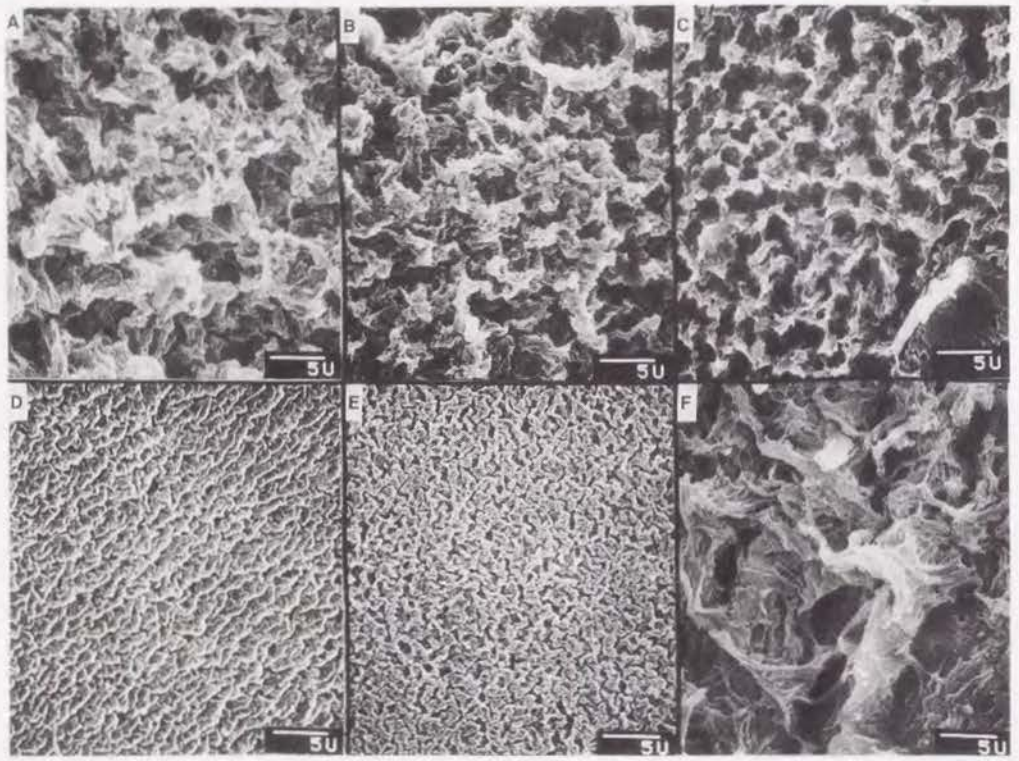

Figure 14. SEM photographs of PVA hydrogel surface crystallized from 20 wt% PVA solution in different mixing ratio of water/DMSO at −20°C for 24 hr.
(A) 100 wt% water ; (B) 20 wt% DMSO
(C) 40 wt% DMSO ; (D) 60 wt% DMSO
(E) 80 wt% DMSO ; (F) 100 wt% DMSO

4. SEM observation of PVA hydrogel

The SEM photographs of PVA hydrogel surfaces are presented in Figure 14. As is seen in Figure 14, the PVA hydrogel surface depends

on mixing ratio of water and DMSO. The PVA hydrogel prepared from 100 wt% water has many pores with sizes larger than 5μm, while in the hydrogel prepared from mixture of water and DMSO pore size decreases with the increasing DMSO concentration and it shows very small regular pores with sizes below 1μm at DMSO 80 wt%.

DISCUSSION

As described above, transparent PVA hydrogels with high water content and high strength could be prepared by low temperature crystallization of PVA solutions in mixed solvents consisting of water and a water−miscible organic solvent. The transparency as well as the mechanical properties of hydrogels depended on the type of organic solvent used, the mixing ratio of water/organic solvent, and the crystallization temperature. Among the organic solvents used here, DMSO gave the highest transparency and the best mechanical properties. This is undoubtedly due to unique solvency of DMSO to PVA.

The properties of diluted PVA solution in mixed solvents from water and DMSO were studied in detail by Imai and his coworkers[2−4]. They found that DMSO is a good solvent of PVA but changes its solvency in a complicated way when water is added to DMSO. A peculiar phenomenon was reported by Yamaura et al. for gelation of concentrated PVA solutions in mixed solvents consisting of water and DMSO[5,6]. Good solvents may give significant solvation to polymer segments, breaking the molecular interaction between the polymer segments. In the case of PVA, the molecular interaction should be

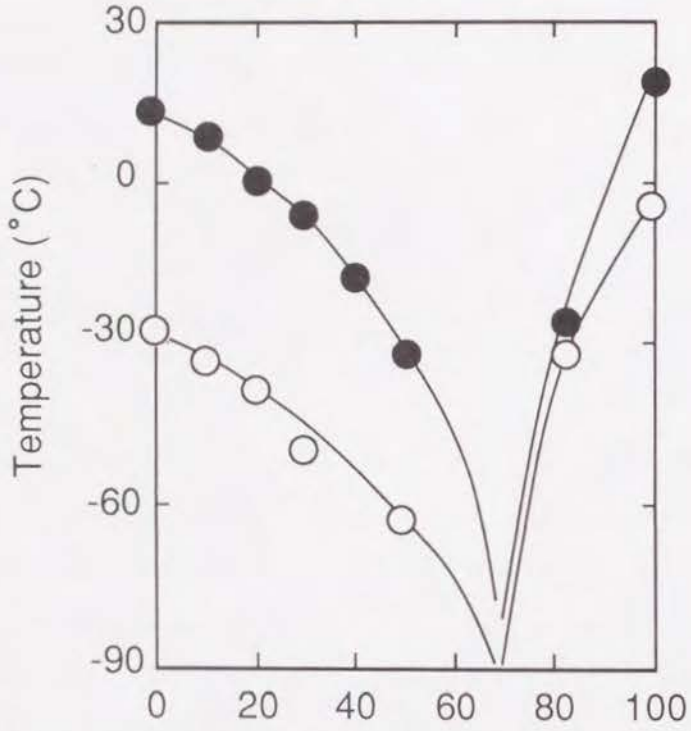

Figure 15. Effect of the DMSO concentration on the melting and freezing temperatures of water/DMSO mixtures without PVA.
(○) freezing temperature ; (●) melting temperature

primarily due to hydrogen bonding which readily leads to crystallization of PVA. Since physical gelation of PVA must be closely related to this crystallization, a too good solvent will not give rise to gelation because of too high solvation, while a too poor solvent may cause very quick crystallization, resulting in formation of large crystallites. It is likely that

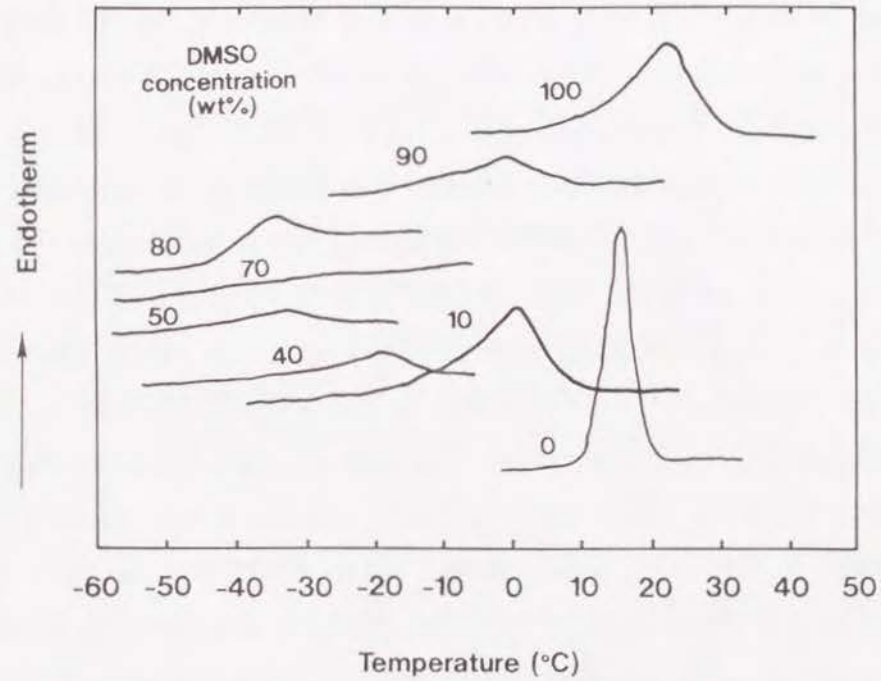

Figure 16. DSC thermograms of water/DMSO mixtures with out PVA.

the crystallites acting as physical crosslinks in PVA gel should be small in size and numerous in number in order to produce a transparent and strong gel. Large crystallites may cause the PVA gel translucent and reduce the effective crosslink density, leading to formation of weak gel.

It is not clear to us why the water/DMSO mixed solvents meet the requirement for appropriate gelation, but there is evidence showing that the water/DMSO mixture is very unique as solvent of PVA. Figure 15 shows melting and freezing temperatures of water/DMSO mixtures

without PVA, determined by DSC. Both the melting and freezing temperatures of the mixed solvent are highly dependent on the mixing ratio of water/DMSO and have a minimum at a DMSO concentration around 70 wt%. A similar trend was also observed for the enthalpy of freezing and melting of the mixed solvent. Figure 16 shows the DSC thermograms of water/DMSO mixtures without PVA. The baseline of each curve is arbitrarily shifted to avoid confusion. The enthalpy change indicates that the mixed solvents are not frozen, at least, in the DMSO concentration ranging from 60 to 70 wt%. Figure 17 shows NMR spectra of PVA solutions in water/DMSO mixtures. NMR spectra of the hydroxy protons of PVA dissolved in 100 wt% DMSO show the three well-separated triad peaks corresponding to isotactic, heterotactic, and syndiotactic PVA sequence. On the contrary, NMR spectra of PVA dissolved in 100 wt% water or in a water/DMSO mixture of 40 wt% DMSO do not show such triad peaks, but they overlap with the hydroxy protons of water. In contrast, NMR spectra of PVA dissolved in mixture of 80 wt% DMSO have the three well-separated triad peaks in spite of the presence of water in the mixed solvent. This result indicates that the 80 wt% DMSO mixture creates a new solvent which quite differs from 100 wt% water or 100 wt% DMSO. The similar result was reported by Horii et al[8].

The transparency of PVA hydrogel depended on the mixing ratio of water/organic solvent and the crystallization temperature. In addition, a suitable mixing ratio and low crystallization temperature were necessary to obtain high transparency. Miyasaka et al. reported occurrence of phase separation of PVA solution[7]. When gelated at room temperature, PVA solution makes a spinodal decomposition before gelation and

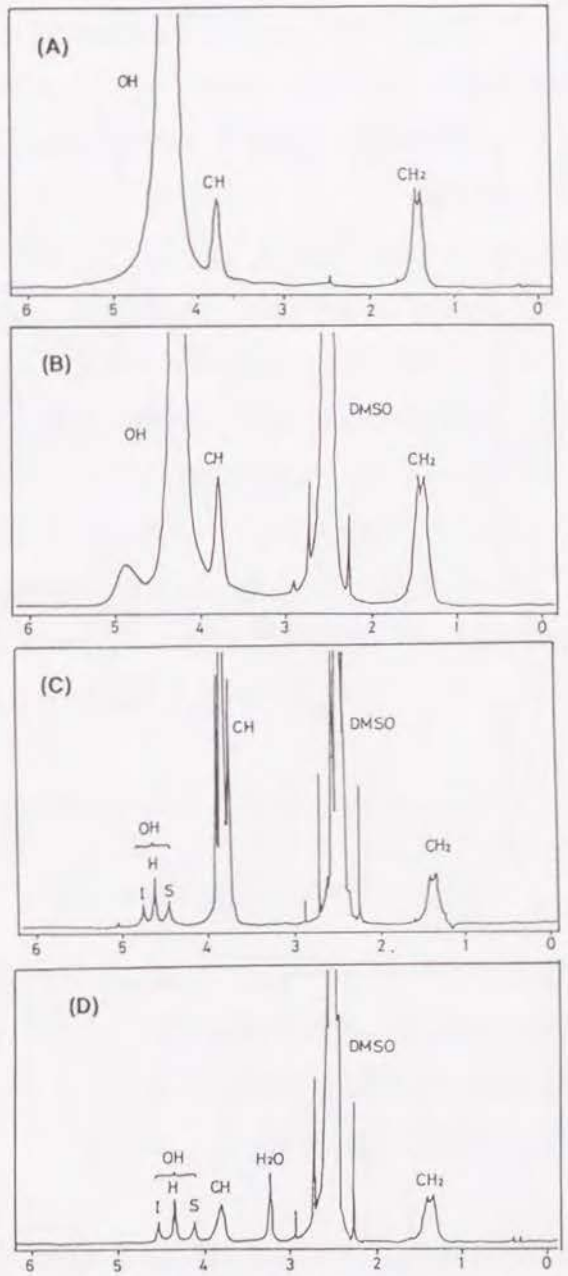

Figure 17. ^{1}H–NMR spectra of PVA solutions in water/DMSO mixed solvents
(A) 100 wt% water ; (B) 40 wt% DMSO
(C) 80 wt% DMSO ; (D) 100 wt% DMSO

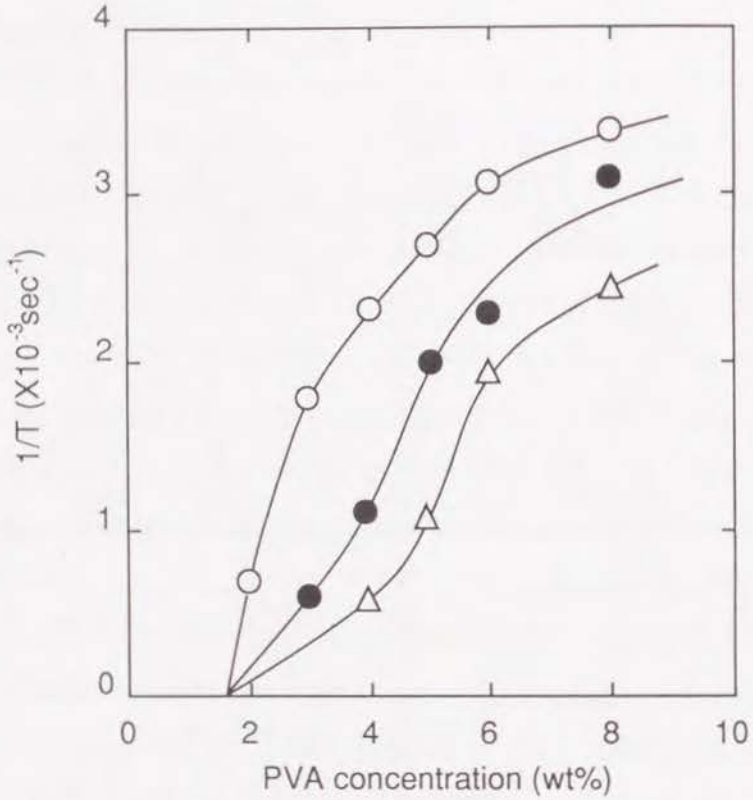

Figure 18. Plot of the reciprocal of gelation time(T) of PVA solution in 80 wt% DMSO at different temperatures as a function of PVA concentration.
(○) −20°C ; (●) −10°C ; (△) 0°C

becomes translucent because a spinodal decomposition rate is higher than its gelation rate. However, at low crystallization temperatures, PVA solution instantly sets to a gel keeping the homogeneous solution state before spinodal decomposition and remains transparent. Actually, as shown in Figure 18, the gelation rate is higher at lower temperature.

Furthermore, as mentioned above, physically crosslinked PVA hydrogels must be formed by creation of PVA microcrystalline regions. Kaji et al. found that for the PVA solution from the water/DMSO mixture the crystalline size became smaller as the crystallization temperature was lower[9]. Then, it can be assumed that when PVA solution is subjected to cooling, many small−sized PVA crystals are formed which act as junctions for physical crosslinks. Consequently, at lower crystallization temperature, PVA solution may set more quickly to a gel under formation of more numerous, smaller microcrystals acting as crosslinks of a three−dimensional gel with high transparency and high strength. In contrast, highly viscous PVA solution will not crystallize at low temperatures due to low segmental motion and hence cannot produce any high strength PVA hydrogel.

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CHAPTER 3

Preparation of poly(vinyl alcohol) hydrogels with low water contents

INTRODUCTION

Bulky PVA hydrogels with large thickness and high mechanical strength were very difficult to prepare unless crosslinking agents were employed until Nambu and Watase found that repeated freezing and thawing of aqueous PVA solution yielded such hydrogels[1–4]. In Chapter 1 and 2, it reported that crystallization of PVA solution at low temperatures also resulted in formation of strong hydrogels even without any cycle of freezing and thawing. Interestingly, the high water content hydrogel was translucent when pure water was used as the solvent, but transparent when the solvent was H_2O/dimethyl sulfoxide(DMSO) mixtures. It is likely that this different optical appearance is ascribed to the difference in size and number of crystallites formed upon crystallization of PVA in aqueous and H_2O/DMSO solution.

When such hydrogels are to be used for practical applications, high mechanical strength and wear resistance are often required but keeping a definite amount of water in the material.

The present study was undertaken to improve the mechanical properties of PVA hydrogels by employing the low temperature crystallization technique. The hydrogels prepared from H_2O/DMSO mixed solvent were subjected to annealing at high temperatures after drying and then to reswelling with water to equilibrium to obtain

hydrogels with low water contents.

EXPERIMENTAL

1. Preparation of PVA hydrogel

The PVA used has viscosity-average degrees of polymerization (DP) of 1,700, 5,000, 7,000, 8,800, and 11,000, all with a degree of saponification of 99.5mol%. First, transparent PVA hydrogels with high water contents were prepared from 6 to 10 wt% PVA solution in a H_2O/DMSO(20/80, w/w) mixed solvent upon cooling the PVA solution to -20°C for 24 hr in glass vessel. The PVA gels formed were immersed in plenty of ethyl alcohol at 20°C for 3 days to exchange the mixed solvent in the gels with ethyl alcohol and then air-dried overnight at room temperature. Following drying, the gels were further kept under vacuum overnight at room temperature to thoroughly remove the organic solvent still remaining in the dried gels, followed by heat treatment in a silicone oil bath kept at 100 to 160°C for 1 to 48 hr. The dried gels had a shape of rod with the diameter of 6mm and the length of 40mm, unless specifically noted. They were finally placed in plenty of water at 37°C for 2 days for rehydration, unless otherwise specified. The water content of the recovered PVA hydrogel was calculated from the equation;

$$\text{water content(wt\%)} = \frac{W_h - W_d}{W_h} \times 100$$

where W_h is the weight of hydrated PVA hydrogel and W_d is the weight of dried PVA hydrogel.

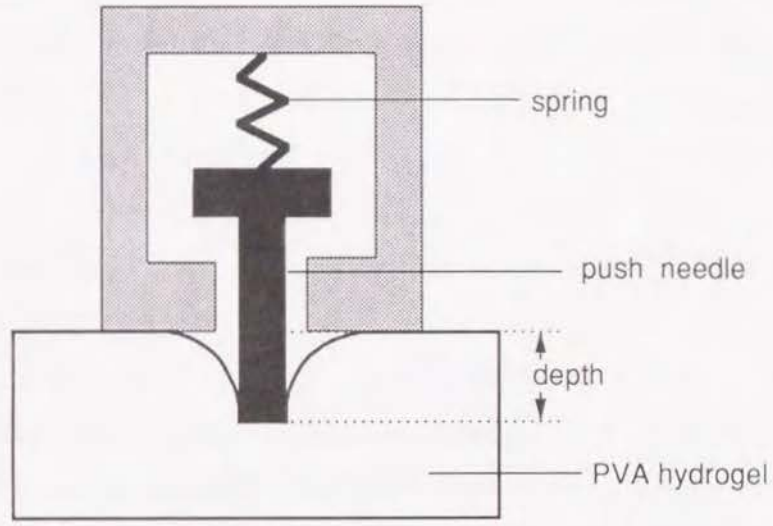

Figure 1. The scheme of hardness tester.

2. Physical measurements

The crystallinity of dried PVA gels was determined from the thermogram area of differential scanning calorimetry(DSC) assuming that the fusion enthalpy of 100% crystalline region of PVA is 37.3 cal/g[5]. Tin(Tm=232°C and ΔH=14.2 cal/g) was used as a standard of the DSC measurement. The tensile strength of wet hydrogels was measured at a tensile speed of 50 mm/min, 25°C, and relative humidity of 65% using Autograph S-100 of Shimadzu Inc., Kyoto, Japan. The samples were stamped out with a dumb-bell test piece in accordance with the JIS criteria. The storage modulus(E') and loss modulus(E") of PVA hydrogels were measured with a dynamic viscoelastometer, DMS-100 of SEIKO Instruments Inc., Tokyo, Japan. The testing was done over a temperature range from 25 to 100°C at a heating rate of 2°C/min and a frequency range from 0.5 to 10 Hz.

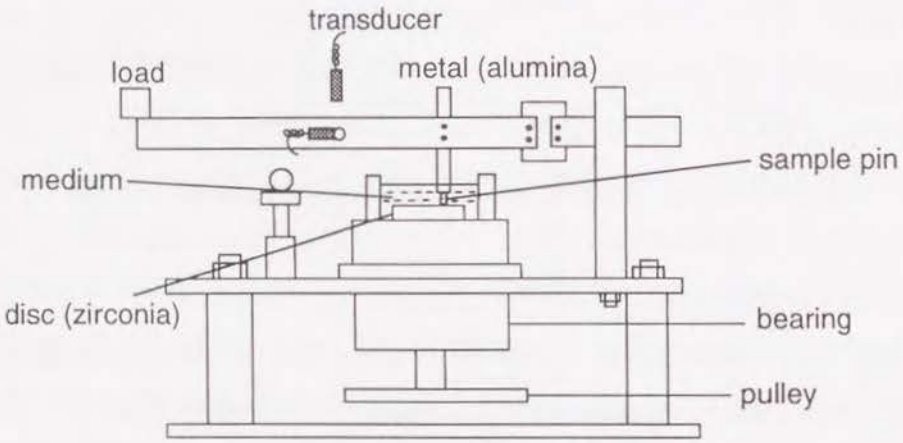

Figure 2. The scheme of "pin–on–disc" wear machine.

The hardness of PVA hydrogel was evaluated by measuring the depth of a needle indenting the hydrogel specimen with Durometer Asker manufactured by Kobunshi keiki Co.,Ltd., Kyoto, Japan. The principle of this tester is shown in Figure 1. The wear test of PVA hydrogels was carried out using a "pin–on–disc" device illustrated in Figure 2. A pin made from the hydrogel specimen with a diameter of 6 mm was pressed against a zirconia disc running at a speed of 50 mm/second under a load of 2 MPa in distilled water containing 1 wt% mucopolysaccharide at room temperature. The wear volume was estimated from the decrease in height of the hydrogel pin by measuring the displacement of transducer after creep had been no more observed. The wear resistance was expressed by the following wear factor;

$$\text{wear factor} = \frac{\text{wear volume } (mm^3)}{\text{Load(N) X sliding distance(mm)}}$$

RESULTS

The PVA hydrogels prepared in the present study were always transparent and had smooth surface in contrast to the translucent PVA hydrogels prepared using 100 wt% water as the solvent of PVA.

1. Annealing effect

To study the influence of hydrogel shape on the mechanical properties, a sheet–type hydrogel with a size of 100mm x 100mm x 2mm was prepared in addition to the rod–type hydrogel which was used throughout this work. The water content of these hydrogels is shown in

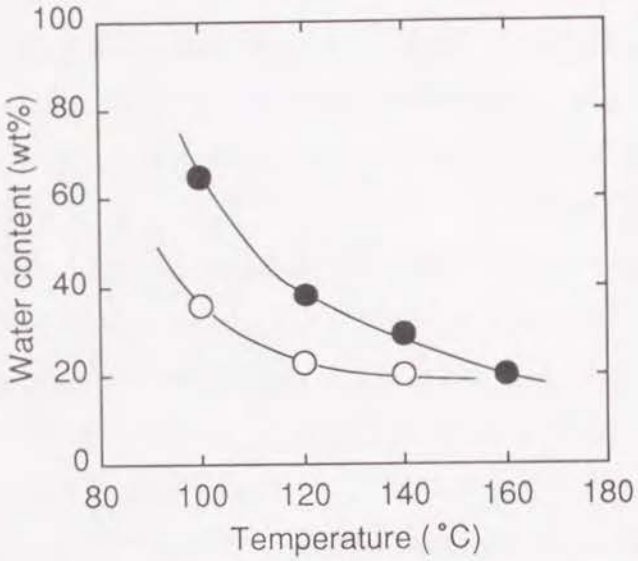

Figure 3. Comparison of the water content of rod– and sheet–type PVA hydrogels annealed at different temperatures for 1 hr. (DP=5,000) (○) rod–type ; (●) sheet–type

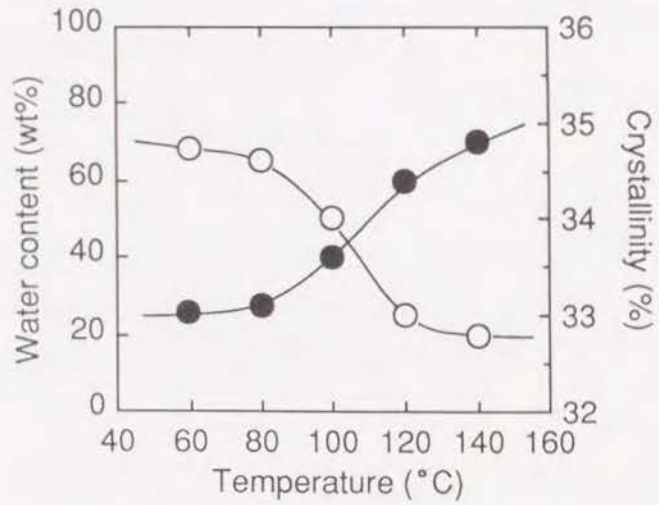

Figure 4. Crystallinities of dry PVA hydrogels and water contents of reswellen PVA hydrogels as a function of annealing temperature. (DP=5,000 and annealing time=1 hr) (○) water content ; (●) crystallinity

Figure 3 as a function of annealing temperature. The annealing time was 1 hr and DP of PVA was 5,000. It is seen that the sheet–type PVA hydrogel needs higher annealing temperature than the rod–type one to attain the same water content. For example, the sheet–type hydrogel of 20 wt% water content was obtained by annealing at 160°C for 1hr, whereas 1 hr annealing at 140°C was sufficient for the rod–type to attain the same water content. Furthermore, when the sheet–type gel prepared from a low DP PVA was annealed at temperatures higher than 100°C, the water content leveled off at 1 hr annealing, whereas the water content of rod–type hydrogel prepared from PVA with high DP was increased with annealing over a longer annealing time(data not shown). Therefore, only rod–type hydrogels were studied in the following experiment.

Figure 4 shows the crystallinity of the hydrogels annealed at different temperatures for 1 hr and the water content of the hydrogels after rehydration. The PVA used had the DP of 5,000. As is seen, the crystallinity of PVA becomes higher with the higher annealing temperature, while the water content of PVA hydrogel is decreased with the rise in annealing temperature. Generally, the water content of hydrogel is inversely proportional to the crystallinity, but the water content of PVA hydrogels prepared from PVA with DP of 11,000 was unexpectedly increased with the annealing time when annealed at 140°C. The result is given in Figure 5. This finding is entirely contrary to the generally observed behavior that high temperature annealing leads to the increased crystallinity which, in turn, reduces the water content of the hydrogel. Also in this case, the crystallinity of dried PVA gels annealed at 140°C was increased with the annealing time, as shown in Figure 6.

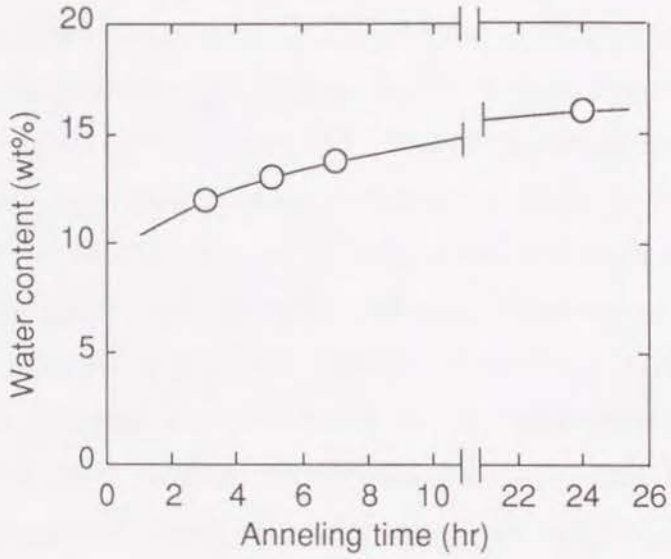

Figure 5. Water content of PVA hydrogels as a function of annealing time. (DP=11,000 and annealing temp.=140°C)

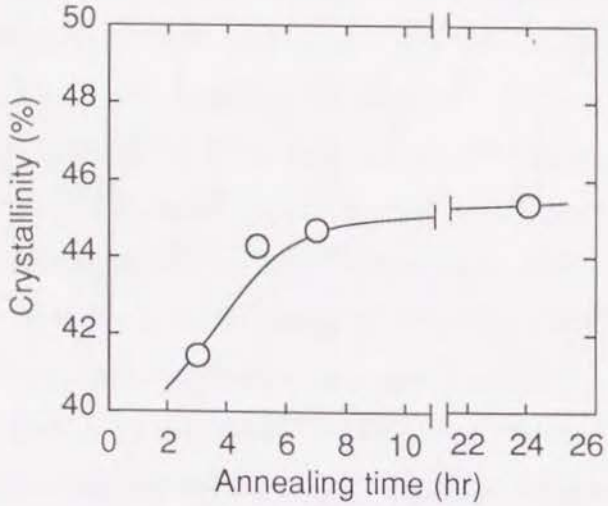

Figure 6. Crystallinities of PVA hydrogels as a function of annealing time. (DP=11,000 and annealing temp.=140°C)

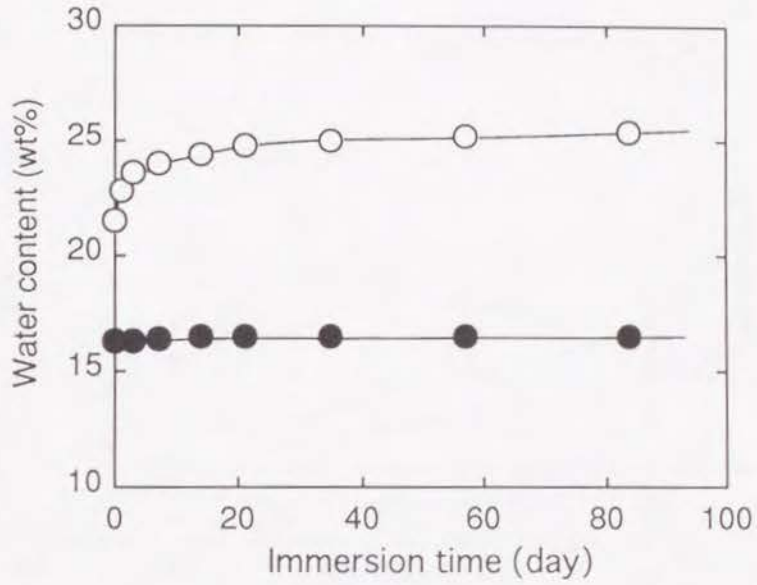

Figure 7. Water contents of PVA hydrogels as a function of immersion time in water at 37°C. (DP=11,000)
(○) annealing at 100°C for 48 hr ; (●) annealing at 140°C for 24 hr

To investigate the stability of the PVA hydrogels in water, hydrogels were prepared from PVA with DP of 11,000, followed by annealing at 100°C for 48 hr or 140°C for 24 hr, and then immersed in water at 37°C. As is evident from Figure 7, where the time dependence of the water content is shown. The water content was increased with elapse of immersion time up to 30 days, but did not change afterward when the PVA hydrogel was annealed at 100°C for 48 hr. In contrast, the water content of the PVA hydrogel prepared by annealing at 140°C for 24 hr practically did not change from the beginning of water immersion up to 85 days. In other words, the PVA hydrogel obtained by annealing at 140°C for 24 hr was stable in water at 37°C at least for 3 months.

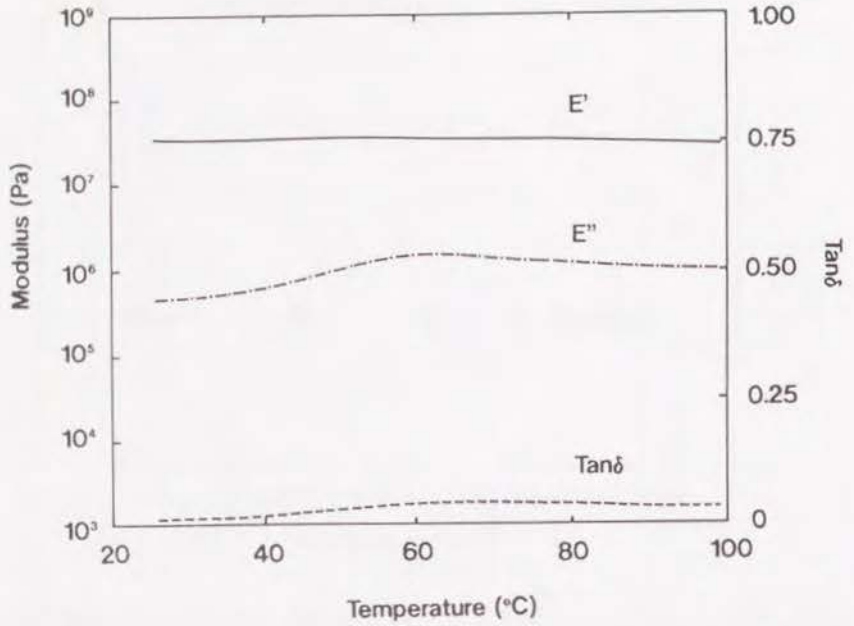

Figure 8. Storage(E') and loss(E") moduli, and Tanδ of PVA hydrogels as a function of temperature.
(DP=5,000 and initial water content=40 wt%)

2. Viscoelastic properties

E' and E" of 40 wt% water content PVA hydrogel prepared from PVA with DP of 5,000 is shown as a function of temperature in Figure 8, together with tanδ. Both E' and E" were independent of the frequency over the range from 0.5 to 10Hz. Apparently, E' and E" of PVA hydrogel did not change over the temperature range from 25 to 100°C. Watase et al. reported that E' of the PVA hydrogels prepared by repeated freezing and thawing was decreased at temperatures higher than 45°C[2,3], but, in contrast to their hydrogels, our transparent PVA hydrogels prepared by the annealing technique had high E' over 100°C, suggesting high thermal stability.

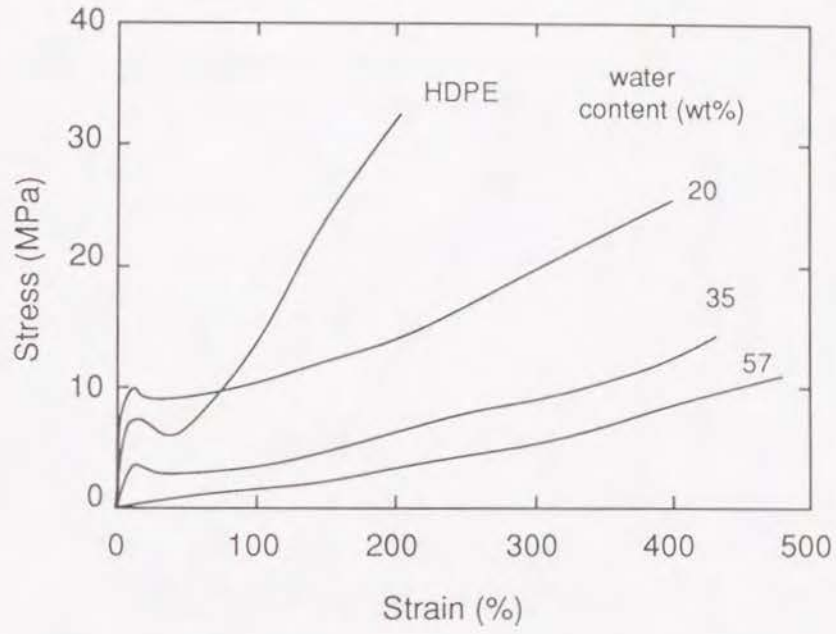

Figure 9. Stress–strain curves of PVA hydrogels with different water contents (DP=5,000) and ultrahigh–molecular weight, high–density polyethylene(HDPE).

3. Mechanical properties

Figure 9 shows typical stress–strain curves of PVA hydrogels with various water contents, prepared by annealing under different conditions. DP of PVA used is 5,000. The stress–strain curve of ultrahigh–molecular–weight, high–density polyethylene (HDPE) is also shown for comparison in Figure 9. The PVA hydrogel with the highest water content exhibited elastic deformation with a high ultimate strength. A yield point was observed for the hydrogels with the water content less than 35 wt%. The yield strength as well as the ultimate strength of PVA hydrogel were increased with the decrease in water content, resulting in higher yield strength than that of HDPE. The tensile strength and dynamic modulus(E' at 25°C) of PVA hydrogels prepared

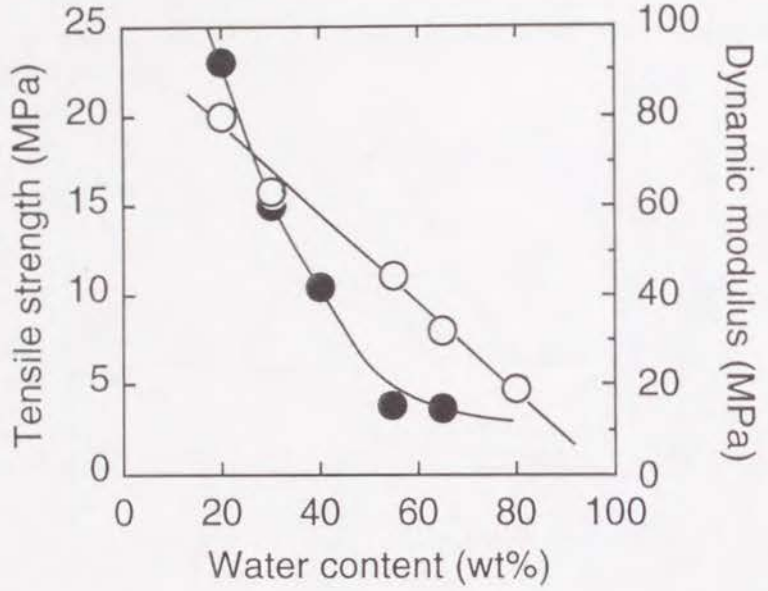

Figure 10. Tensile strengths and dynamic moduli of PVA hydrogels as a function of water content. (DP=5,000)
(○) tensile strength ; (●) dynamic modulus

from PVA with DP of 5,000 are shown in Figure 10 as a function of water content. The tensile strength of the PVA hydrogel was almost linearly decreased with the increasing water content. On the other hand, the dynamic modulus of PVA hydrogel was steeply decreased with an increase in water content. For instance, the modulus of PVA hydrogel with 55 wt% water content was approximately 1/6 of that of 20 wt% water content. Figure 11 shows the effect of DP of PVA on the tensile strength and dynamic modulus of PVA hydrogels. All of them were prepared so as to have a similar water content around 20 wt%. As is seen, the dynamic modulus was gradually increased with DP of PVA, while the tensile strength remained almost unchanged, regardless of the DP of PVA.

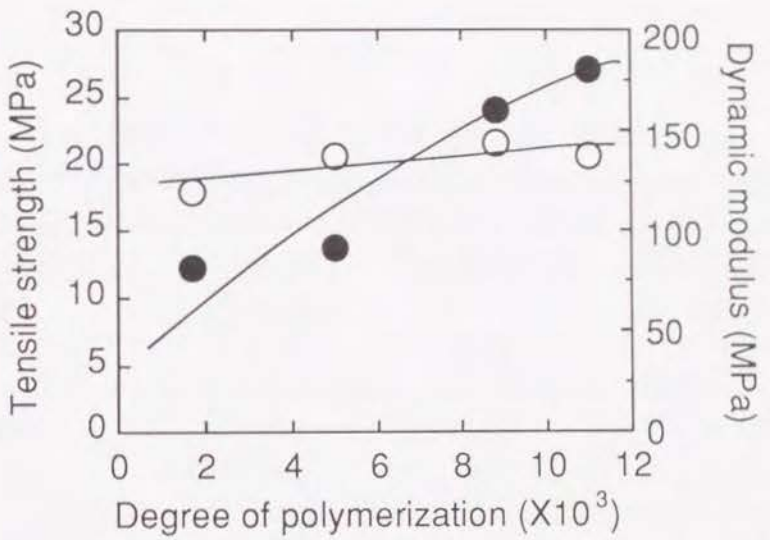

Figure 11. Tensile strengths and dynamic moduli of PVA hydrogels as a function of DP of PVA. (water content=20 wt%)
(○) tensile strength ; (●) dynamic modulus

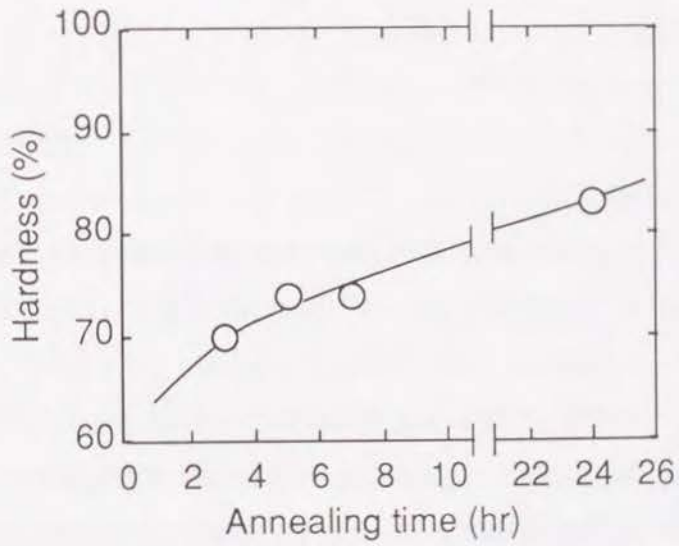

Figure 12. Hardness of PVA hydrogels as a function of annealing time. (DP=11,000 and annealing temp.=140°C)

Table 1. Hardness of PVA hydrogels (DP=11,000).

Annealing temperature (°C)	Annealing time (hr)	Water content (wt%)	Hardness (%)
100	24	22	60
	48	24	61
120	24	16	73
	48	18	73
140	24	16	83
	48	18	93

4. Hardness and wear

Table 1 summarized the hardness and water content of rod-type PVA hydrogels prepared from PVA with DP of 11,000 under various annealing conditions. The water content of hydrogels was slightly increased with the annealing time when annealed at 100 and 120°C, although the hardness remained virtually constant. However, prolonged annealing at 140°C gave rise to increased hardness. The hardness of rod-type hydrogels prepared from PVA with DP of 11,000 is shown in Figure 12 as a function of annealing time. The wear factor, expressed in

Table 2. Wear factors of PVA hydrogels with different DP's and a ultrahigh-molecular-weight, high-density polyethylene(HDPE).

Polymer	DP	Water content (wt%)	Wear factor ($mm^3/N \cdot mm$)
PVA	5,000	22	11.5×10^{-6}
	7,000	16	10.8×10^{-6}
	11,000	16	1.2×10^{-6}
HDPE	Ca. 100,000	0	1.6×10^{-6}

a unit of $mm^3/N \cdot m$, is summarized in Table 2. The wear factor became lower with the increasing DP and the decreasing water content of PVA hydrogel. When DP of PVA was 5,000 and the water content was 22 wt% , the wear factor of PVA hydrogel was 11.5×10^{-6}, whereas that of hydrogel with the water content of 16 wt% and DP of 11,000 was as low as 1.2×10^{-6}, which was lower than that of HDPE.

DISCUSSION

PVA belongs to a group of conventional polymers with repeating units of simple chemical structure, but is a little different from others because of possession of hydroxyl groups which allow crystallization and dissolution in water through hydrogen bonding. Owing to this

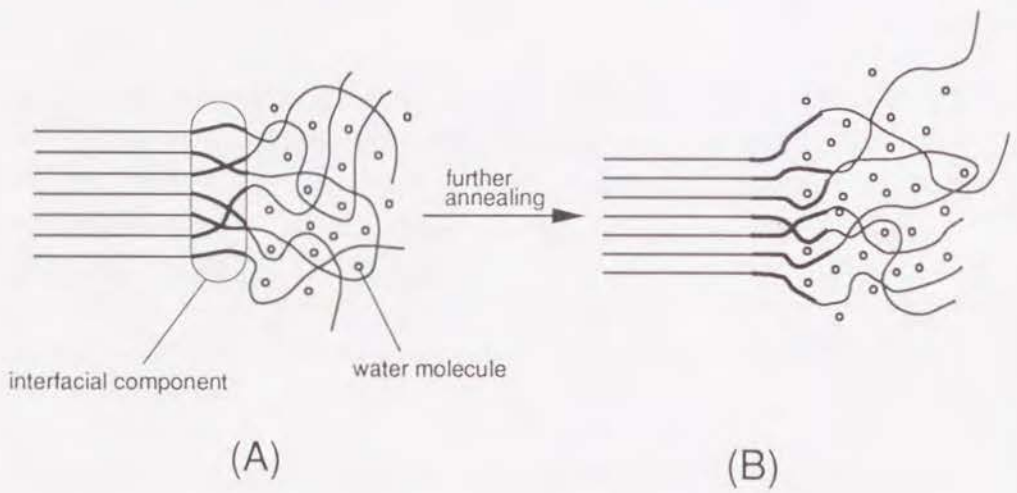

Figure 13. A structure model of annealed and the water-reswellen PVA hydrogel.
(A) short annealing ; (B) long annealing

unique property, PVA has been widely used in industry in the form of fiber, film, and aqueous solution. However, hydrogels from PVA have not yet found any practical applications. If their mechanical properties are greatly improved, it will be used, for example, as sealer and shock absorber in the place where water is always present more or less. A component for artificial joints in orthopedic surgery is also a promising application.

As demonstrated above, mechanical properties of PVA hydrogels including hardness and wear factor could be greatly improved with annealing of the dried hydrogel, although the water content was decreased. The water content of this PVA hydrogel prepared by physical

crosslinking should be greatly governed by the crystallization of PVA molecular chains[6]. It is widely thought that the water content of hydrogels prepared from crystalline polymers is decreased with the annealing time because the crystallinity must be increased by annealing. However, as shown in Figure 5 and Table 1, the water content of PVA hydrogel was increased with the extension of annealing time. This finding is not understandable if we simply assume that prolonged annealing increases the crystallinity of PVA and hence reduces the water content of hydrogel. The increased hardness by prolongation of annealing time shown in Figure 12 may be explained in terms of increased crystallinity. It is, however, unlikely that the water content of hydrogels physically crosslinked by microcrystallites is a simple function of overall crystallinity of the hydrogel. In the present study, the crystallinity was evaluated from the DSC result which does not give any information on the size and number of microcrystallites, but only on the overall crystallinity which is the product of size and number of microcrystallites. It seems reasonable to assume that the water content of PVA hydrogel is directly related to the number density of crystallites, but not to the overall crystallinity which must have a large influence an the hardness and wear of the PVA hydrogel.

The increased water content of hydrogel with longer annealing may be explained in terms of phase structure of crystalline polymers. Bergmann et al. and Horii et al. reported from their NMR studies[7-10] that polyethylene has an interfacial component between the crystalline region and the non-crystalline region. The model of hydrogel structure is illustrated in Figure 13, referring to their findings. When annealing time is short, the interfacial component may be still present in PVA as

shown in Figure 13 (A). As annealing time becomes longer, the interfacial component in PVA will be changed into the crystalline region and the non-crystalline region as depicted in Figure 13 (B). Consequently, both the crystalline and the non-crystalline region may be increased, resulting in enhanced water content and hardness of the PVA hydrogel with the annealing time.

It seems probable that a subtle difference in PVA microstructure among hydrogels has a large effect on the difference in water content between the sheet and the rod hydrogel seen in Figure 3 as well as on the difference in wear factor of hydrogels with 16 wt% water content between DP of 7,000 and 11,000.

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CHAPTER 4

Preparation of sticky poly(vinyl alcohol) hydrogels

INTRODUCTION

A number of methods have been reported for preparation of PVA hydrogels, including chemical methods[1] using covalent crosslinking agent such as glutaraldehyde and boric acid; physical methods[2] using complexing agents such as titanium, aluminum, manganese, and copper; and radiation methods[3-5] using γ-ray, electron beam, and ultraviolet light. In Chapter 1 and Chapter 2, a physical method to prepare PVA hydrogels from water alone or a mixture of water and organic solvent by low temperature crystallization of concentrated PVA solutions were reported. Although most of the hydrogels prepared with these methods are high in water content and excellent in mechanical properties, all of them are not sticky and have poor elasticity below 0°C, because the water in the gel freezes below 0°C. Furthermore, the water in PVA hydrogel readily vaporizes at room temperature. If PVA hydrogels having high stickiness and good water-holding ability can be prepared, they would find applications as biomaterials, for instance, in transdermal therapeutic systems. This Chapter describes a preparation method and properties of sticky PVA hydrogel.

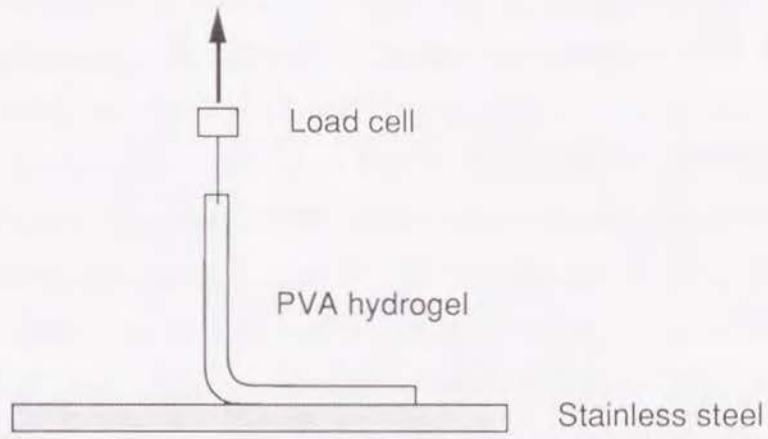

Figure 1. Schematic diagram for the 90° peel strength measurement of PVA hydrogels.

EXPERIMENTAL

1. Preparation of PVA hydrogel

The PVA used in this study is atactic and commercially available with a viscosity-average degree of polymerization of 1,700 and a degree of saponification of 99.5 mol%. An aqueous PVA solution with polymer concentrations from 10 to 30 wt% was mixed with an aqueous $CaCl_2$ solution of different concentrations at 110°C for 1 hr in an autoclave. After the temperature of the admixed solutions was lowered to 60°C, they were placed on a glass plate to a thickness around 1mm and allowed to stand at −20°C for 24 hr to prepare PVA hydrogels containing $CaCl_2$. The weight concentration of $CaCl_2$ in the hydrogels is not expressed based on the total gel, but on the $CaCl_2$ solution before mixing with the PVA solution for simplicity.

2. Physical measurements

The water-holding ability of PVA hydrogel was estimated from the weight change occurring when left at 25°C in a relative humidity of 65%. The degree of swelling of PVA hydrogel was determined by weighing the PVA hydrogel before and after immersion in water at 37°C. The melting temperature of the PVA hydrogel was measured by Ferry method[6] at a heating rate of 1 °C/min. The tensile strength and the elongation at break were measured with a tensile tester at a cross-head speed of 50 mm/min at 25°C and a relative humidity of 65%. Dumb-bell test pieces in accordance with JIS specifications were cut from the gel sheet of 1mm thickness. The peel strength of the PVA hydrogel on a stainless steel was measured by the 90° peel strength method depicted in Figure 1.

The state of hydration of Ca ions in aqueous $CaCl_2$ solution was estimated by differential scanning calorimetry(DSC). Following cooling to −80°C, the samples were heated at the rate of 10 °C/min.

RESULTS

1. Water-holding ability of PVA hydrogel

The weight change of wet PVA hydrogels containing $CaCl_2$ of different concentrations observed at 25°C and a relative humidity of 65% is shown in Figure 2. As is apparent, the weight change of PVA hydrogels ceases after 1 day, regardless of the $CaCl_2$ concentration, but the extent of weight change becomes less prominent with the increasing $CaCl_2$ concentration. The PVA hydrogel without $CaCl_2$ releases almost all of its water after 1 day, whereas the PVA hydrogel prepared from 30

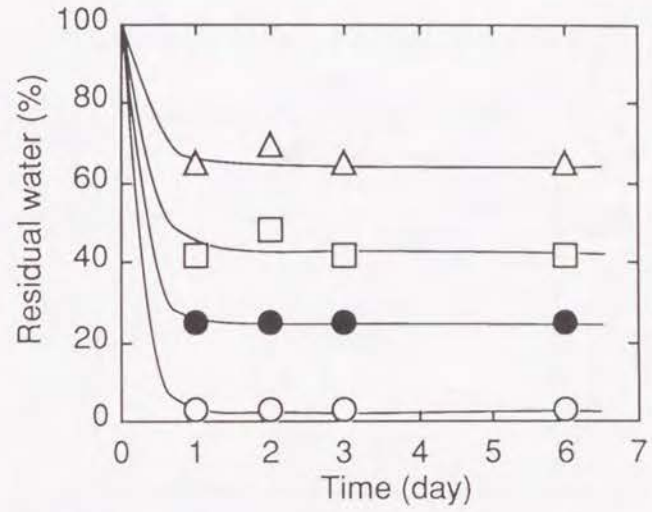

Figure 2. Residual weight of 15 wt% PVA hydrogels as a function of drying time.

[$CaCl_2$] : (○) 0 wt% ; (●) 10 wt% ; (□) 20 wt% ; (△) 30 wt%

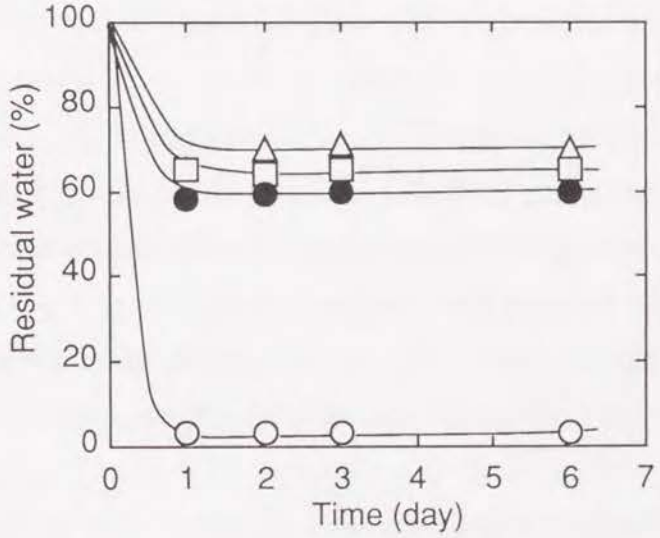

Figure 3. Residual weight of PVA hydrogels as a function of drying time.

[PVA] : (●),13 wt% ; (□),18 wt% ; (△),20 wt%

(○),0 wt% $CaCl_2$, 15 wt% PVA

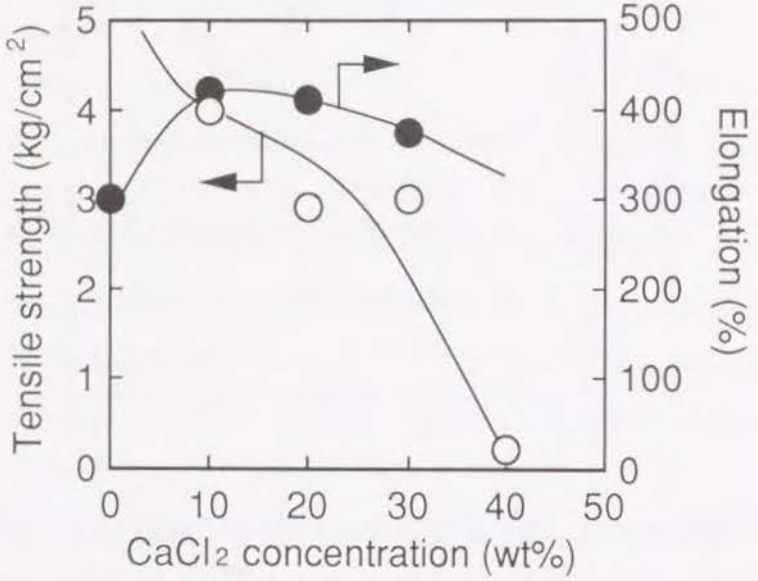

Figure 4. Tensile strength and elongation of 15 wt% PVA hydrogels as a function of $CaCl_2$ concentration.

wt% $CaCl_2$ aqueous solution maintains 65% of its water after 6 days. Figure 3 shows the result of weight change of PVA hydrogels of various water contents, the $CaCl_2$ concentration being kept at 30 wt%. Apparently, the weight change is slight and independent of the PVA concentration. It follows from Figures 2 and 3 that the water-holding ability is dependent on the $CaCl_2$ concentration, but independent of the PVA concentration in hydrogel, provided $CaCl_2$ is present.

2. Tensile properties of PVA hydrogel

The tensile strength and the elongation of the PVA hydrogels were measured as a function of $CaCl_2$ concentration. The result is given in Figure 4. As is seen, the tensile strength as well as the elongation are dependent on the $CaCl_2$ concentration. The tensile strength decreases

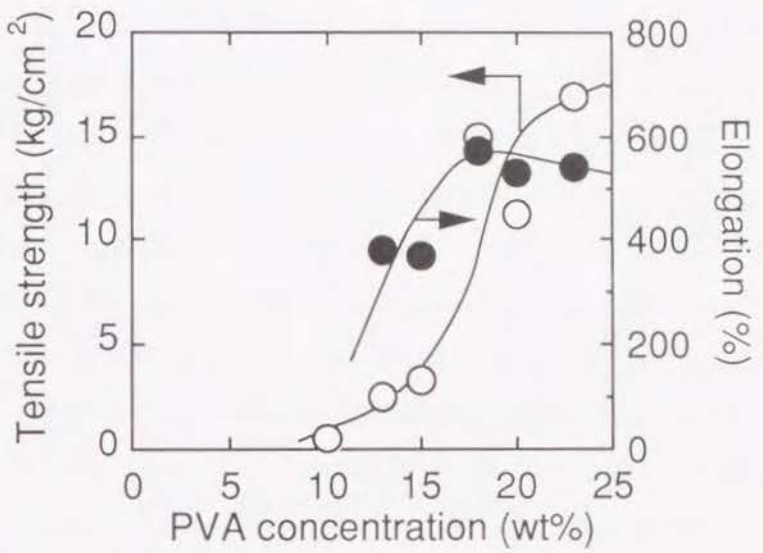

Figure 5. Tensile strength and elongation of PVA hydrogels containing 30 wt% $CaCl_2$ as a function of PVA concentration.

drastically with the increasing $CaCl_2$ concentration, but still has a high value such as 3 kg/cm^2 at 30 wt% $CaCl_2$ concentration. On the other hand, the elongation becomes maximum at 10 wt% $CaCl_2$ concentration. This value is about 1.5 times as high as the elongation of PVA hydrogel without $CaCl_2$. The dependence of tensile strength and elongation on the PVA concentration is shown in Figure 5. The $CaCl_2$ concentration was kept at 30 wt%. The tensile strength slowly increases with the PVA concentration up to 15 wt%, but drastically increases when the PVA concentration is in the range from 15 to 25 wt%. At a PVA concentration of 25 wt%, the tensile strength reaches 17 kg/cm^2, which is about 3 times as high as that of a PVA hydrogel with the PVA concentration of 15 wt%.

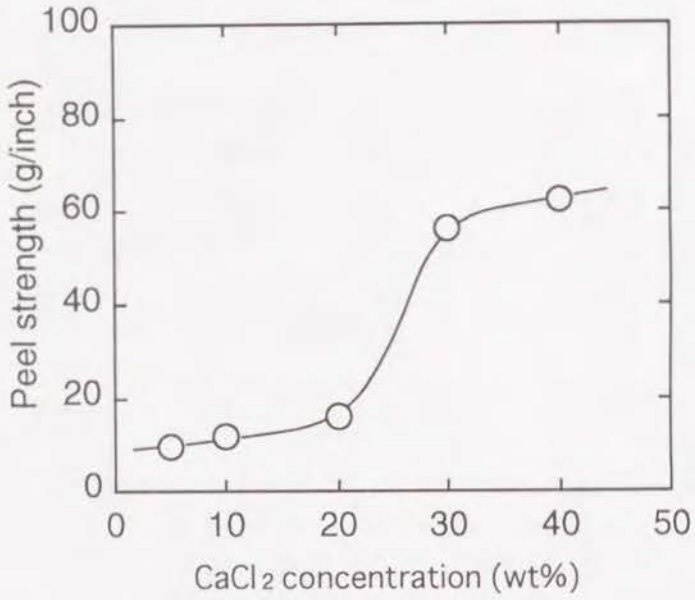

Figure 6. Peel strength of 15 wt% PVA hydrogels a as a function of $CaCl_2$ concentration.

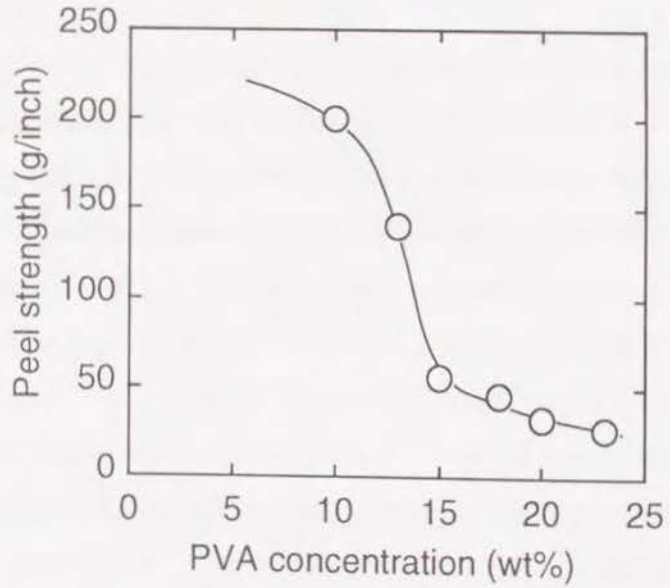

Figure 7. Peel strength of PVA hydrogels containing 30 wt% $CaCl_2$ as a function of PVA concentration.

3. Peel strength of PVA hydrogel

Figures 6 and 7 show the peel strength of PVA hydrogels as a function of $CaCl_2$ and PVA concentration, respectively. The peel strength measurement was conducted to have a quantitative measure of the hydrogel stickiness. The peel strength is higher as the surface of PVA hydrogel become more sticky. As can be seen, the concentration dependence of the peel strength is opposite to that of the tensile strength. The peel strength drastically increases when the $CaCl_2$ concentration increases from 20 to 30 wt%, but exhibits a gradual increase when $CaCl_2$ is further added. The peel strength of PVA hydrogel prepared from 30 wt% $CaCl_2$ is 55 g/inch, about 4 times as high as that of PVA hydrogel prepared from 20 wt% $CaCl_2$. As is obvious from the dependence of the peel strength on the PVA concentration shown in Figure 7, the peel strength steeply increases with the decreasing PVA concentration, reaching 200 g/inch at a PVA concentration of 10 wt%, when the $CaCl_2$ concentration is kept at 30 wt%.

4. Swelling and melting temperature of PVA hydrogel

The degree of swelling of PVA hydrogels is given in Figure 8 as a function of immersion time in water kept at 37°C. Apparently, the degree of swelling reaches a maximum at 1 day and afterwards gradually decreases for all the PVA hydrogels. The $CaCl_2$ concentration significantly influences the swelling change of PVA hydrogel, especially when the $CaCl_2$ concentration increases from 20 to 30 wt%. This suggests that the physical structure of PVA hydrogel also changes at $CaCl_2$ concentrations ranging from 20 to 30 wt%. No leaching of PVA was observed during the swelling experiment.

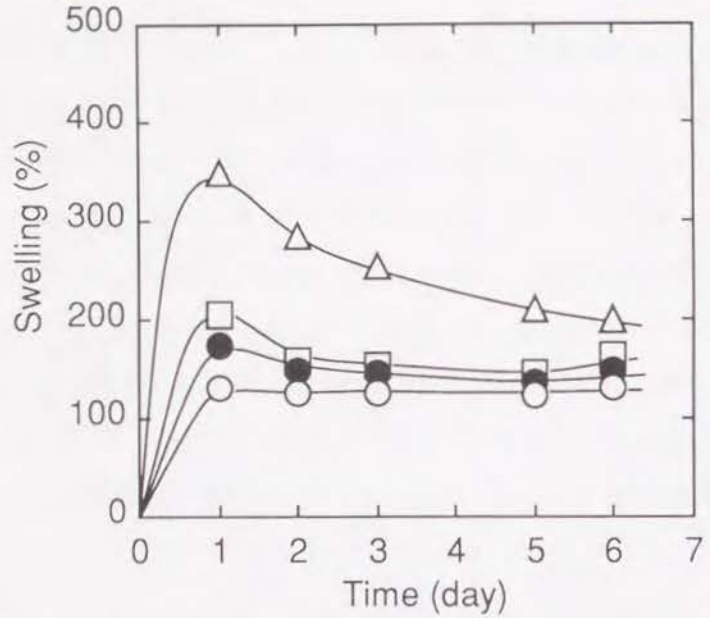

Figure 8. Time course of swelling change in water at 37°C for 15 wt% PVA hydrogels containing $CaCl_2$ of different concentrations. [$CaCl_2$] : (○) 0 wt% ; (●) 10 wt% ; (□) 20 wt% ; (△) 30 wt%

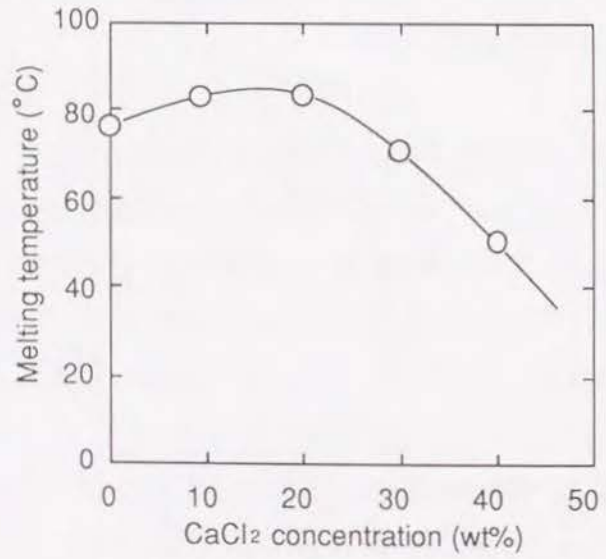

Figure 9. Melting temperature of 10 wt% PVA hydrogels as a function of $CaCl_2$ concentration.

Figure 9 shows the melting temperature of PVA hydrogels with different $CaCl_2$ concentrations. The melting temperature increases very slightly up to 20 wt% $CaCl_2$ and is not greatly different from that of PVA hydrogel without $CaCl_2$. However, at $CaCl_2$ concentrations higher than 20 wt%, the melting temperature decreases drastically and becomes 50°C at the $CaCl_2$ concentration of 40 wt%. The dependence of melting temperature of hydrogels on the $CaCl_2$ concentration is similar to that of elongation shown in Figure 4.

DISCUSSION

As described above, sticky PVA hydrogels could be obtained from aqueous PVA solutions containing $CaCl_2$. The peel strength, which is a measure of stickiness, depended strongly on the $CaCl_2$ concentration, similar to the tensile strength. Furthermore, the dependence of tensile strength and peel strength on the $CaCl_2$ concentration were in opposite directions to each other. As a compromise, sticky PVA hydrogels with high strength could be obtained at concentrations of 30 wt% $CaCl_2$ and 15 wt% PVA, as comparison of Figure 4 with Figure 6 or Figure 5 with Figure 7 indicates. In addition, the above results clearly indicate that the physical structure of PVA hydrogel changes in the $CaCl_2$ concentration range from 20 to 30 wt%. This was further evidenced by the results of swelling and melting. The decrease in swelling by water immersion for longer than 1 day may be due to further crystallization of PVA chains in water at 37°C.

Divalent transient metallic salts such as titanium, zirconium, copper, and cobalt, can create complexes with PVA chains by

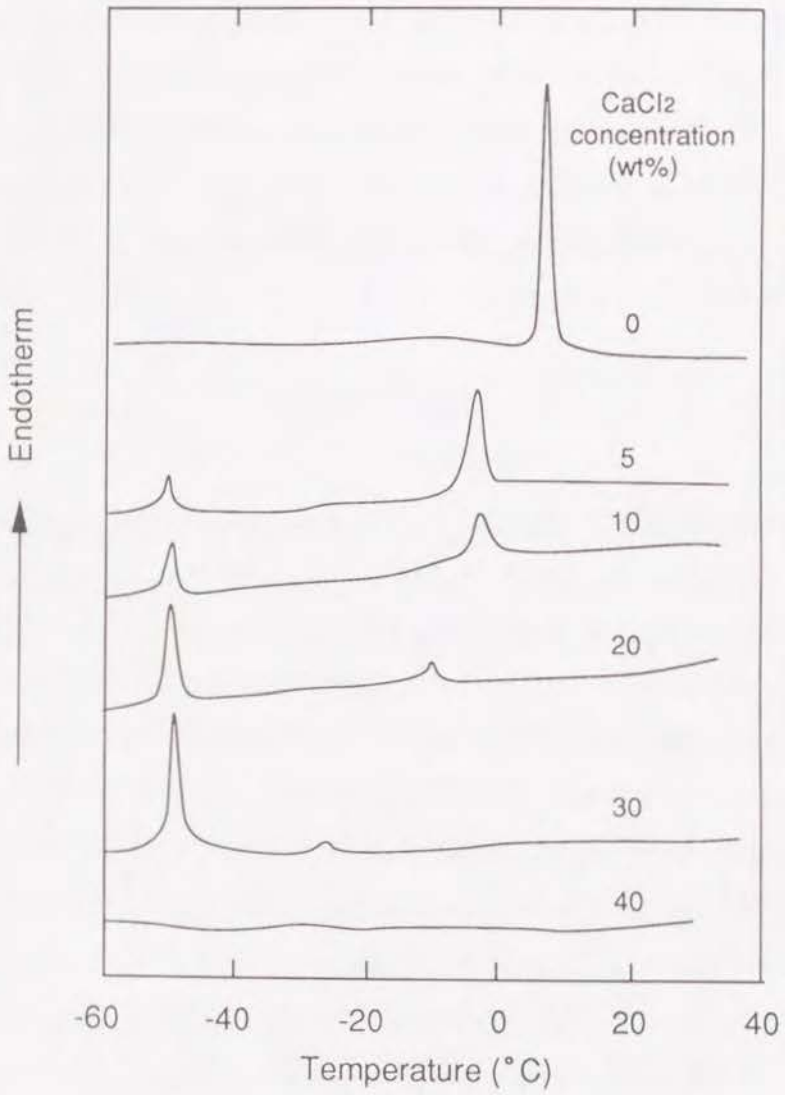

Figure 10. DSC thermograms of water–$CaCl_2$ mixtures without PVA.

coordinated bonds, resulting in water–insoluble gel formation[2]. To the contrary, when monovalent metallic salts such as sodium, potassium, thallium, and lithium, are added to aqueous PVA solution, stable hydrogel is not formed, because these metals are precipitants of PVA. On the other hand, divalent metallic salts such as magnesium and calcium neither precipitate PVA nor create strong complex bonds with PVA, probably because of strong interaction of the metallic ions with water. Consequently, these divalent metallic ions may form only weak crosslinks between the PVA chains, creating the sticky transparent PVA hydrogel. The water–holding ability of PVA hydrogel containing $CaCl_2$ might be associated with the high deliquescence and moisture regain of Ca ion, but this seems not to be the case as demonstrated below.

To study the hydration of Ca ion in aqueous $CaCl_2$ solution without PVA, DSC was performed and is shown in Figure 10. The endothermic peak of aqueous $CaCl_2$ solution splits into two in the $CaCl_2$ concentration range from 5 to 30 wt%. As the $CaCl_2$ concentration increases, the first melting peak appearing around 0°C shifts to lower temperatures but the second melting peak around −50°C remains unchanged. On the other hand, the peak area of the first melting temperature decreases with the increasing $CaCl_2$ concentration, whereas the peak area of the second melting temperature increases with the increasing $CaCl_2$ concentration. This result clearly indicates that the state of hydration of Ca ion in aqueous $CaCl_2$ solution changes with the $CaCl_2$ concentration. When the $CaCl_2$ concentration is low, lots of free water molecules may exist in aqueous $CaCl_2$ solution to freeze at or near 0°C. As a result, these solutions would produce the PVA hydrogels having physical properties similar to those prepared from water alone

without $CaCl_2$. On the other hand, highly concentrated solutions of $CaCl_2$ may contain too little free water to freeze at or below 0°C because of the significant interaction between Ca ions and water, leading to formation of a sticky PVA hydrogel with excellent water-holding ability and high strength.

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CHAPTER 5

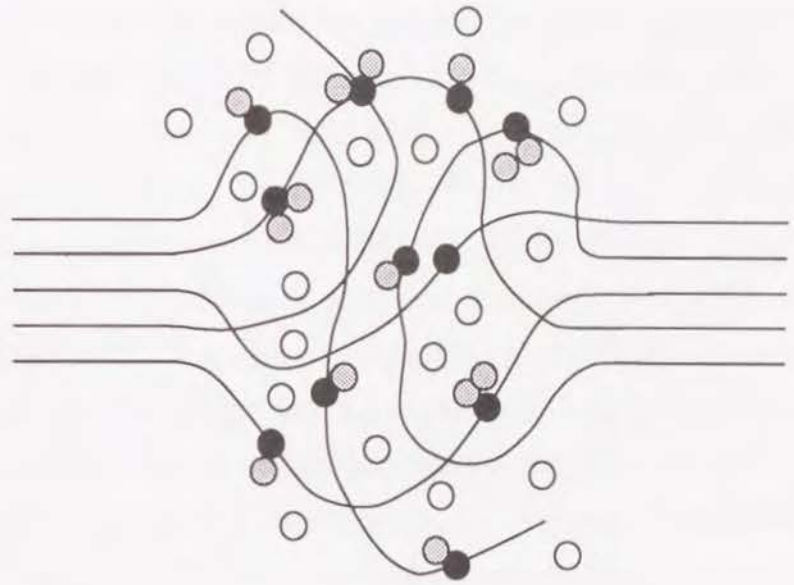
Microstructure of poly(vinyl alcohol) hydrogels predicted from differential scanning calorimetric study

INTRODUCTION

It has been known that such hydrogels as having a wide range of water content and mechanical strength can be prepared from PVA through physical and chemical crosslinking[1-6]. In Chapter 2, it have demonstrated that low temperature crystallization of PVA solutions made from water/organic solvent mixtures produces transparent hydrogels with high water contents and excellent mechanical properties.

It is essential to study the dependence of the hydrogel microstructure on the variables in the hydrogel preparation. However, very few physical means are available that are applicable to the identification of the microstructure of the hydrogels containing water. Among them are light scattering, X-ray diffraction, and NMR, but they cannot give clear information on the hydrogel microstructure, because the gel is in the water-swollen state.

As the most dominant feature of hydrogels over other polymeric materials is inclusion of water in the materials, it is conceivable that a study on the physical state of water in the hydrogel might provide us with useful suggestions on the microstructure of the hydrogels. The structure of water in hydrogels and water adsorbed to polymers has been investigated by numerous workers[7-25]. According to their results, the



(●); Bound water

(○); Free water

(◎); Intermediate water

Figure 1. Presumed arrangement model of water in hydrogel with microcrystallites.

water in hydrogel can be generally classified into three species; non-freezing bound water, freezing intermediate water, and freezing free water. Figure 1 illustrates a presumed model for the water structures in hydrogel with microcrystallites. Since the property of the bound water is greatly different from that of the two other waters, the amount of the bound water can be measured with various methods such as isothermal

adsorption and desorption[7,8], dilatometry[9,10], nuclear magnetic relaxation spectroscopy[11-15], and differential scanning calorimetry (DSC)[16-22].

The present study employs the most widely used DSC method to predict the microstructure of PVA hydrogels prepared with three different methods.

EXPERIMENTAL

1. Hydrogel preparations

The PVA used has a viscosity-average degree of polymerization (DP) of 1,700 with a degree of saponification of 99.5 mol%, unless otherwise specified.

1-1. Chemical crosslinking with glutaraldehyde

Aqueous PVA solution with the polymer concentration range from 10 to 30 wt% was prepared at 110°C using an autoclave. After lowering the temperature of the solution to 30°C, it was mixed with different concentrations of glutaraldehyde(GA) and 0.5M HCl, poured into a glass vessel, and then left at 30°C for 24 hr to allow crosslinking reaction to proceed.

1-2. Annealing of film

10 wt% aqueous PVA solution was poured into a glass vessel, followed by air-drying at room temperature for 1 week to obtain a PVA film. After annealing in a silicone oil bath kept at 80 to 160°C for 1hr, the film was placed in plenty of water at 37°C for 2 days for hydration.

1-3. Low temperature crystallization

Not only the PVA with DP of 1,700 but also those with DP of 3,200 and 5,000 were used for the low temperature crystallization of PVA. First, homogeneous PVA solution with a concentration of 15 wt% was prepared by heating an organic solvent/water mixture containing PVA powder at 120°C for 2hr in N_2 atmosphere. The organic solvents to be mixed with water included glycerin(GC), ethylene glycol(EG), and dimethyl sulfoxide(DMSO). After the temperature of PVA solution was lowered to 60°C, it was cast on a glass plate and allowed to stand at -20°C for 24 hr to promote PVA crystallization. The resulting PVA gel was immersed in ethyl alcohol at room temperature for 3 days and air-dried overnight. Following drying, the gel was further subjected to vacuum drying overnight to remove the organic solvent remaining in the gel, followed by heat treatment in a silicone oil bath kept at 80 to 140°C for 2 hr. The annealed dry gel was placed in water at 37°C for 2 days for rehydration.

2. DSC measurement

The DSC measurement on hydrogels was performed using a thermal analyzer, DT-30 of Shimadzu Inc., Kyoto, Japan. The hydrogel sample was sealed between two pans using a pan crimper. The weight of hydrogel sample ranged from 8 to 20mg. After cooling to -80°C with liquid nitrogen, the frozen hydrogel sample was heated at a rate of 10 °C/min in helium gas. The heat of fusion was calculated from the thermogram area using pure water as a standard of the DSC measurement.

RESULTS

1. Effect of crosslinking method

As an example, the DSC curves obtained for the gels prepared by low temperature crystallization of PVA solution in H_2O/DMSO(20/80, w/w) are shown in Figure 2, together with that of pure water. It is seen that the PVA gel with the equilibrated water content of 66 wt% has a single endothermic peak at temperature a little lower than 0°C, while the hydrogels with the water contents of 49 and 27 wt% exhibit two endothermic peaks at temperature close to the freezing point of pure water and much lower than 0°C. The former and the latter peak will call f_I and f_{II}, respectively. The presence of two peaks in DSC curve of hydrated gels has been reported by many researchers and it is widely intermediate water existing in the hydrogel, respectively. The non-freezing bound water is also present in the hydrogel, although its presence cannot be recognized in the DSC curve because of its non-freezability or non-fusibility.

Table 1 gives the concentration of the three different waters estimated under the assumption that the heat of fusion of the frozen free water(f_I) and the frozen intermediate water(f_{II}) are 79.7 and 69.0 cal/g accepted that the f_I and the f_{II} peak are assigned to the free and the H_2O[26], respectively. The concentration of the non-freezing bound water was calculated by subtracting the concentration of the frozen waters from the total concentration of water. It is interesting to note that the concentration of the bound water is practically not dependent on the total water content of the hydrogels, so far as they are prepared either by the low temperature crystallization or by the annealing method. This is

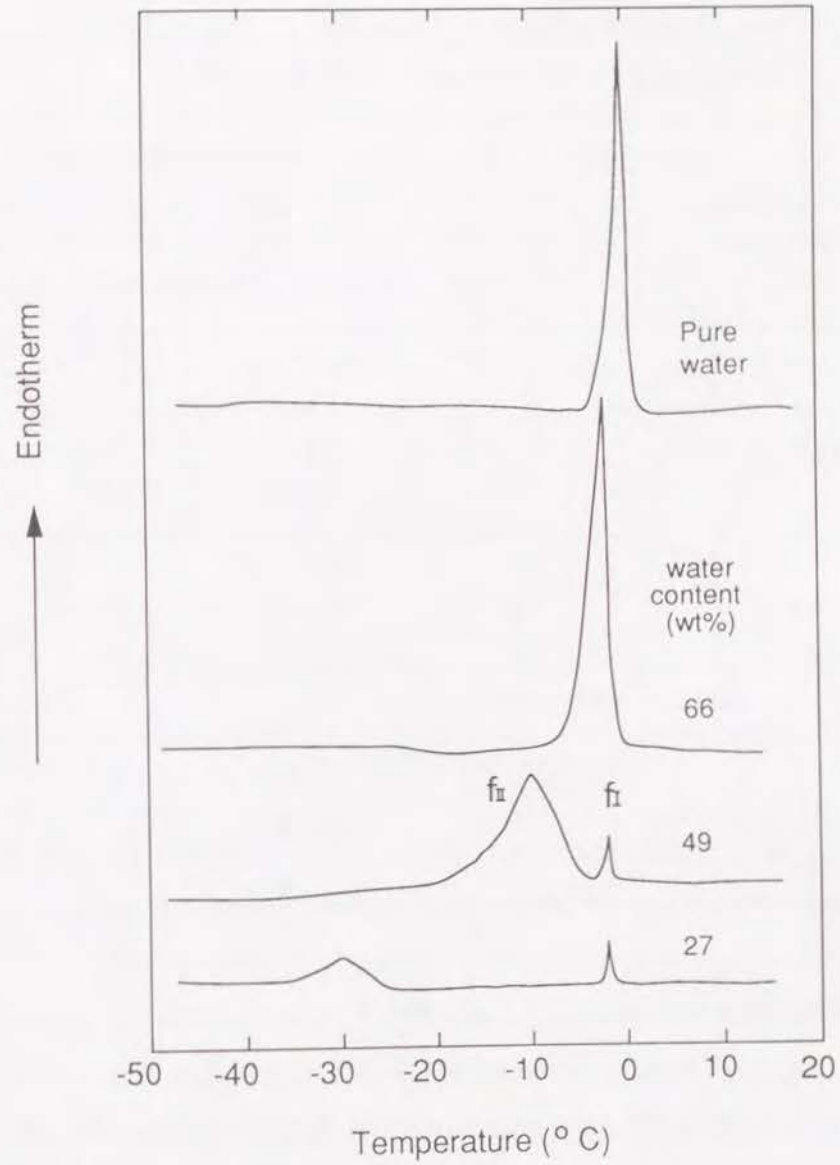


Figure 2. DSC thermograms of frozen waters in the PVA hydrogels prepared by low temperature crystallization of PVA solution in H_2O/DMSO(20/80, w/w) mixed solvent. (DP=5,000)

Table 1. The concentration of three kinds of water in PVA hydrogels prepared with different methods (DP=1,700).

Preparation method	Water content (wt%)	Water concentration (mol/mol of repeating unit)		
		free(f_I)	intermediate(f_{II})	bound
Low temperature crystallization	68	4.78	–	0.35
	52	2.18	–	0.46
	40	0.14	1.22	0.27
	17	0.04	0.12	0.34
Film annealing	69	4.13	–	1.35
	58	0.20	1.73	1.37
	54	0.18	1.24	1.45
	36	0.17	–	1.21
Glutaraldehyde crosslinking	85	13.90	–	0.18
	76	7.79	–	0.54
	69	4.13	–	1.49

in contrast with the hydrogel prepared by the chemical crosslinking. Clearly, the low temperature crystallization gel has less non-freezing bound water than the gel prepared by the annealing of cast film. It would be most reasonable to compare the hydration difference among the hydrogels prepared with different methods at a similar total water content. When the comparison is made at a water content around 68–69 wt%, it is apparent from Table 1 that there is no significant difference in the free water content among the three hydrogels, whereas those prepared by low temperature crystallization contains much less non-

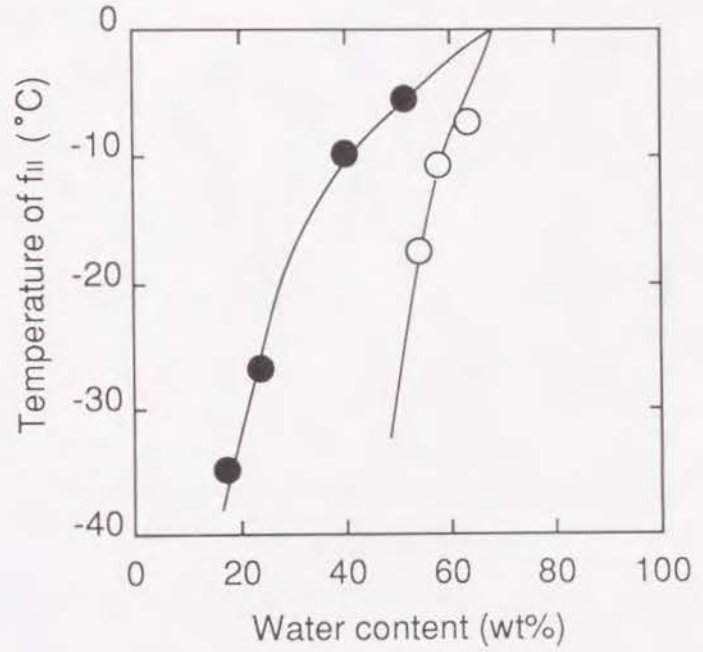


Figure 3. Melting temperature of the frozen water(f_{II}) in PVA hydrogels prepared by film annealing and low temperature crystallization methods as a function of water content. (○) film annealing ; (●) low temperature crystallization

freezing bound water than those prepared by annealing and chemical crosslinking.

Freezing of the hydrated water in hydrogels can be more clearly compared when the peak temperature of melting and the total heat of fusion are plotted against the total water content of the hydrogels. The results are given in Figures 3 and 4, respectively. Crosslinking of PVA with GA could not produce any hydrogels having water content lower

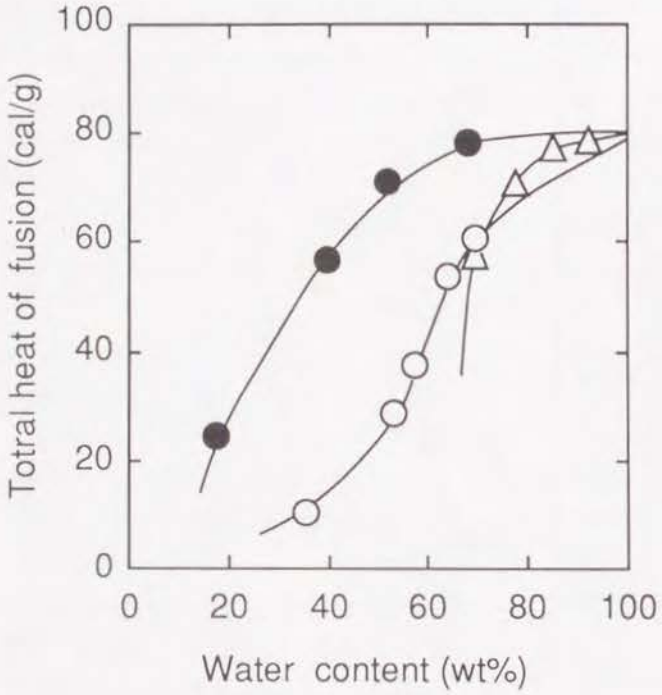


Figure 4. Total heat of fusion of frozen waters in PVA hydrogels prepared with various methods as a function of water content.
(○) film annealing ; (●) low temperature crystallization
(△) gultaraldehyde crosslinking

than 65 wt%. As can be seen in Figures 3 and 4, there is a significant difference in both the temperature of f_{II} and the total heat of fusion among the preparation methods of hydrogel. Apparently, the low temperature crystallization technique gives larger heat of fusion with higher f_{II} temperature than the annealing one. This suggests that the frozen intermediate water in the hydrogel prepared by the low temperature crystallization may have more ordered structure than that of the hydrogel prepared by the annealing method.

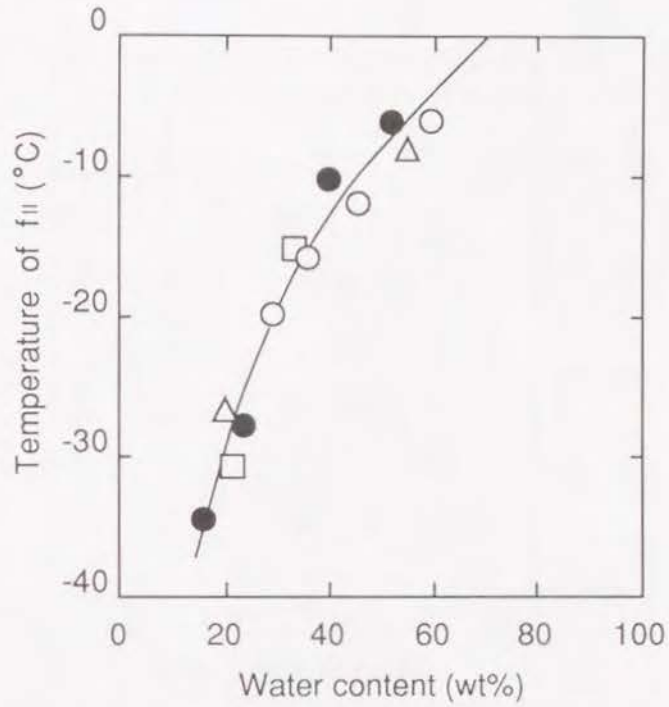


Figure 5. Melting temperature of the frozen water(f_{II}) in PVA hydrogels prepared from different solvents by low temperature crystallization method as a function of water content.
(○) 100 wt% water ; (●) 80 wt% DMSO
(□) 60 wt% GC ; (△) 60 wt% EG

2. Effect of organic solvent

Other mixed solvents than the H_2O/DMSO(20/80, w/w) mixture also could produce hydrogels when the PVA solutions prepared from the mixed solvents were subjected to crystallization at low temperatures. In the present work, H_2O/GC(40/60, w/w) and H_2O/EG(40/60, w/w) were employed as the mixed solvent for PVA in addition to the H_2O/DMSO(20/80, w/w) mixture. The results obtained from the DSC study on the hydrogels prepared using these mixed solvents are given in

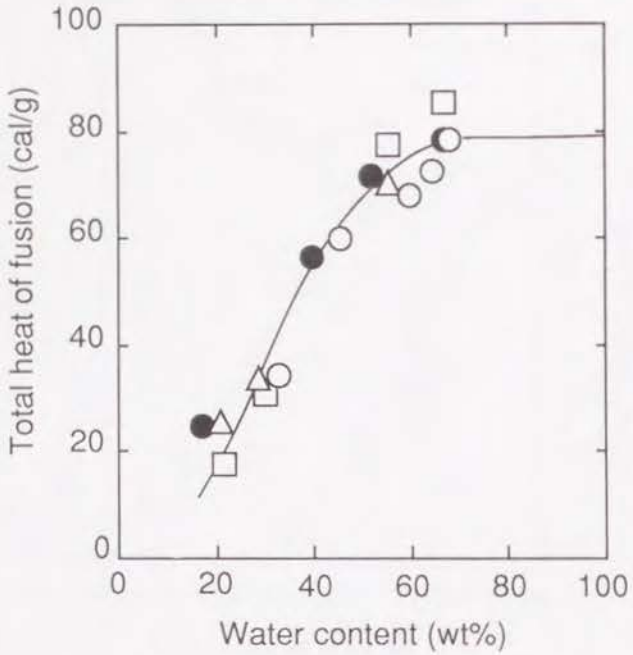


Figure 6. Total heat of fusion of frozen waters in PVA hydrogels prepared from different solvents by low temperature crystallization as a function of water content.
(○) 100 wt% water ; (●) 80 wt% DMSO
(□) 60 wt% GC ; (△) 60 wt% EG

Figures 5 and 6, together with those of hydrogels made by crystallization of PVA solution in 100 wt% water at −20°C. It is obvious that all the hydrogels have the same f_{II} temperature and the same heat of fusion, irrespective of the solvent composition, if the water content of the hydrogels is identical. It should be pointed out that the hydrogels prepared from 100 wt% water give the DSC results identical to those of other gels prepared from H_2O/organic solvent mixtures, although the former gels are translucent in contrast to other transparent hydrogels.

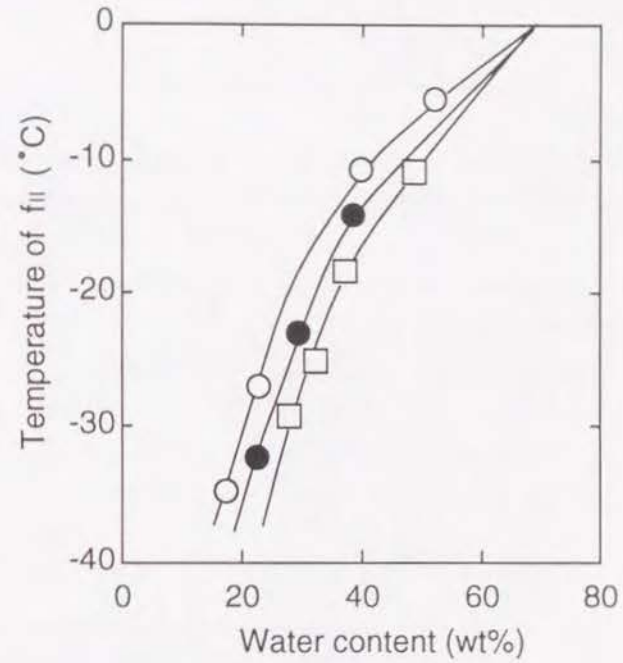


Figure 7. Melting temperature of frozen water(f_{II}) in PVA hydrogels prepared from PVA of different DP's by low temperature crystallization as a function of water content.
(○) 1,700 ; (●) 3,200 ; (□) 5,000

3. Effect of degree of polymerization

Figures 7 and 8 show the f_{II} melting temperature and the total heat of fusion estimated from the DSC curves of the hydrogels of PVA with different DP's. The hydrogels were prepared by low temperature crystallization from the H_2O/DMSO(20/80, w/w) mixture. As can be seen from Figure 8, DP of PVA clearly influences the total heat of fusion of the frozen waters in the hydrogels. Comparison at a similar water content reveals that the hydrogel prepared from PVA with higher

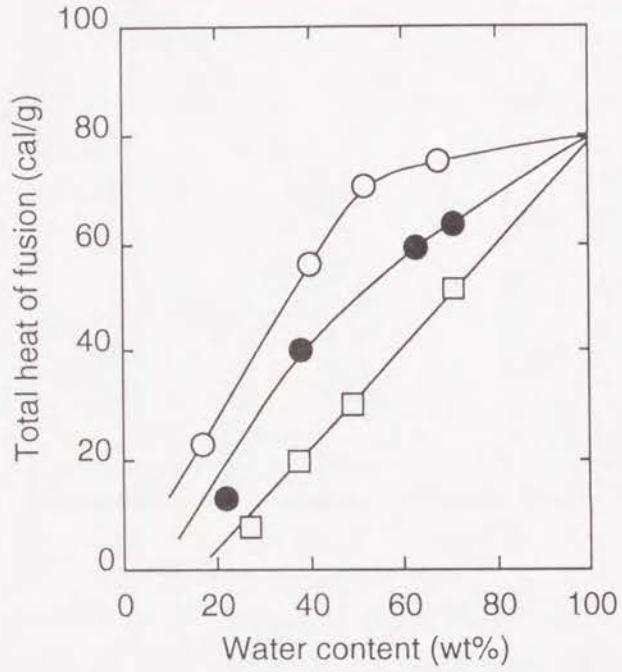


Figure 8. Total heat of fusion of frozen waters in PVA hydrogels prepared from PVA of different DP's by low temperature crystallization as a function of water content.
(○) 1,700 ; (●) 3,200 ; (□) 5,000

DP has lower total heat of fusion. Although not as significant as the heat of fusion, f_{II} is also dependent on DP of PVA. The frozen intermediate water seems to have less ordered structure as DP of PVA increases. The concentration of free, intermediate, and bound waters is given in Table 2. It appears that the concentration of non-freezing bound water becomes higher as DP of PVA increases, whereas the reverse tendency is observed for the intermediate water.

Table 2. The concentration of three kinds of water in hydrogels prepared from PVA of different DP's by low temperature crystallization.

DP	Water content (wt%)	Water concentration (mol/mol of repeating unit)		
		free(f_I)	intermediate(f_{II})	bound
1,700	68	4.78	–	0.35
	52	2.18	–	0.46
	40	0.14	1.22	0.27
	17	0.04	0.12	0.34
3,200	69	4.59	–	0.84
	63	3.27	–	0.89
	38	0.09	0.80	0.63
	22	0.05	0.06	0.56
5,000	66	3.34	–	1.41
	49	0.10	0.98	1.27
	37	0.06	0.35	1.02
	33	0.05	0.27	0.89
	27	0.04	0.05	0.80

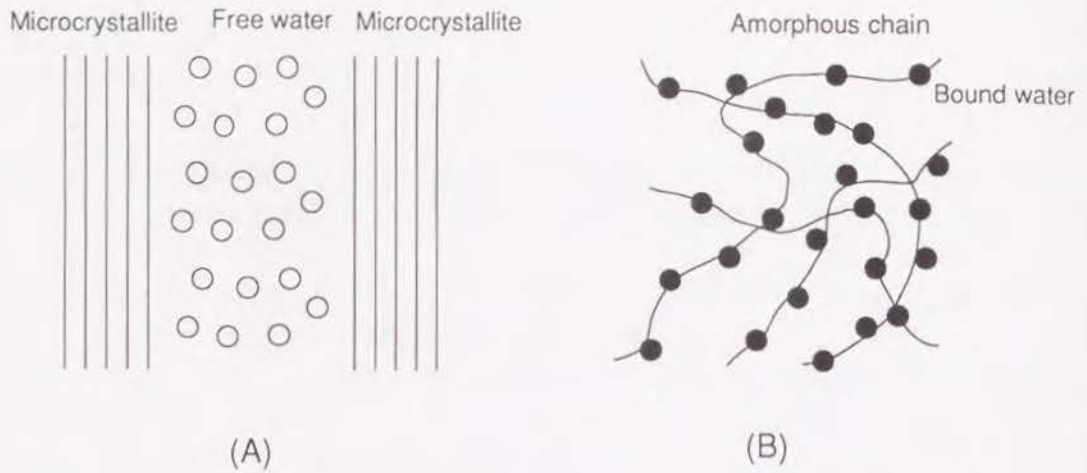


Figure 9. Two extreme microstructure models of PVA hydrogel with the water content around 50 wt%.

DISCUSSION

The results described above support the model illustrated in Figure 1 with respect to the structure of water in hydrogels. Although the relative concentration of the free, intermediate, and bound waters as well as the phase structure of these three waters must be closely related to the microstructure of hydrogel, it is still not easy to clearly figure out the possible structure of the hydrogels from the above DSC results.

For prediction of the microstructure of the hydrated PVA gel it may be helpful to propose two extreme cases as represented in Figure 9. The one is composed of PVA microcrystallites and the free water alone, while the other model consists of completely amorphous PVA chains and the water bound to the chains alone. The real structure of the PVA hydrogel containing lots of small microcrystallites may be intermediate

between the two extremes. It seems probable that, among the hydrogels with a similar total water content, the microstructure of hydrogel with higher concentration of the free water or higher f_{II} temperature may be closer to that shown in Figure 9 (a), while the hydrogel with higher concentration of the non-freezing bound water or lower f_{II} temperature may have the microstructure closer to that given in Figure 9 (b).

Based on the above assumption one can predict the microstructure of PVA hydrogels as follows. When a PVA hydrogel is prepared from homogeneous aqueous solution of PVA at room temperature with the use of chemical crosslinking agent such as GA, the resulting hydrogel virtually contains no PVA semicrystallites to allow the presence of high concentration of free water so far as the total water content is higher than about 80 wt%. It is interesting to note that, if each repeating unit of PVA is assumed to bind one water molecule, the water content solely due to the bound water amounts to approximately 30 wt%. The hydrogel prepared by simple annealing of dried PVA film at temperatures between the glass transition temperature and the melting point may have lots of small crystallites as illustrated in Figure 10 (a). As a result, the hydrogel formed upon hydration of the annealed film may contain a high concentration of bound water. On the other hand, the remarkably high concentration of the intermediate water in the hydrogels obtained by low temperature crystallization of PVA solution from water/organic solvent mixtures suggests that there is a relatively high large free space between the PVA microcrystallites larger than those of the annealed film. Thus, the microstructure of the hydrogel prepared with the low temperature crystallization method may be schematically represented as in Figure 10 (b). The microstructure of this hydrogel is not significantly

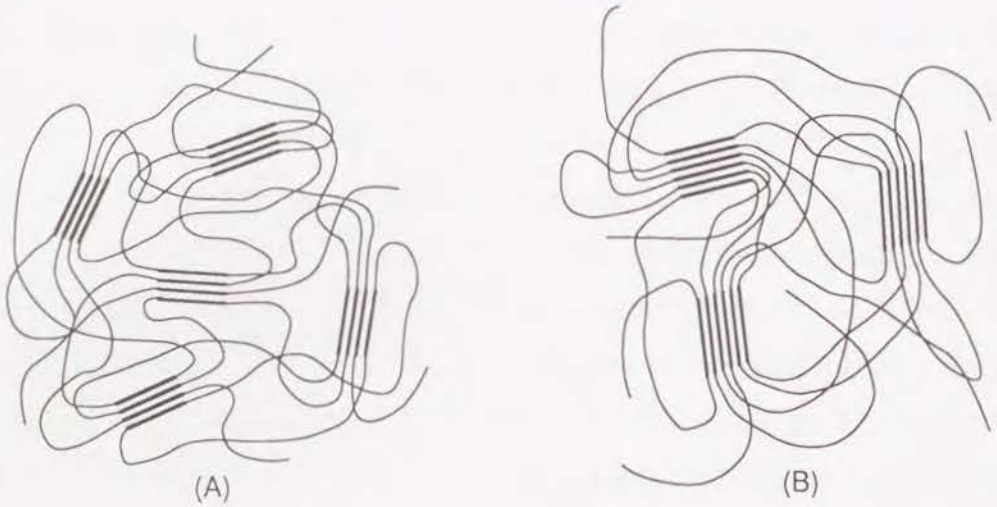


Figure 10. The structure model of different PVA hydrogel predicted from the DSC study.
(A) Gel by film annealing
(B) Gel by low temperature crystallization

influenced by the nature of the organic solvent used for the mixed solvent preparation, as indicated in Figure 5 and 6. However, DP of PVA should have an effect on the microstructure of the hydrogel, as the results in Figures 7 and 8 and Table 2 suggest. The decrease in free water content with the increasing DP of PVA implies that the concentration of the free PVA chains which are not involved in crystallite formation is higher as the DP of PVA becomes higher. This is in good accordance with the previous result that the hydrogel prepared from PVA of higher DP yielded fiber with higher tensile strength, because the higher strength should be attributed to higher concentration of tie molecules connecting the PVA microcrystallites as free chains.

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CHAPTER 6

Protein adsorption on poly(vinyl alcohol) hydrogels

INTRODUCTION

As a functional material, much attention has been paid to hydrogel and various hydrogel materials have been synthesized. Also, PVA hydrogel has been studied as biomaterial[1–4], since high water content and high strength hydrogel was obtained from PVA by repeating the freezing and defreezing of the concentrated aqueous PVA solutions[5,6] or by low temperature crystallization of aqueous PVA solution.

When hydrogel is used as biomaterial, protein adsorption on the material surface becomes a very important factor because it influences the efficacy of the hydrogel as biomaterial. For example, adsorption of serum proteins on a material surface has been proved to play an important role in formation of thrombus and, therefore, the interaction between serum proteins and material surface has been extensively investigated[7]. Furthermore, a major cause for clouding of worn contact lenses is known to be protein adsorption on its surface[8–11]. Protein adsorption also leads to bacterial infection, resulting in giant papillary conjunctivitis[12]. Thus, protein adsorption has been a serious problem for contact lenses of long term wearing as well as oxygen permeability and hence protein adsorption on contact lens materials have been investigated by several research groups[13,14].

This Chapter deals with protein adsorption on translucent and

transparent PVA hydrogels.

EXPERIMENTAL

1. Preparation of hydrogels

A commercial PVA was used which has a viscosity-average degree of polymerization of 1,700 and a degree of saponification of 99.5 mol%. The translucent PVA hydrogel was prepared by −20°C freezing of the aqueous solution in the PVA concentration range from 10 to 30 wt% for 24 hr, followed by slow crystallization at 5°C for 24 hr. The transparent PVA gel was prepared by low temperature crystallization of PVA solution of different concentrations at −20°C for 24 hr in a mixture consisting of water and DMSO(20/80, w/w). The gel obtained as a result of PVA crystallization was placed in flowing water at room temperature for 4 days to exchange DMSO included in the gel with water. PHEMA was synthesized by copolymerization of HEMA and 1,4-butanediol methacrylate for comparison.

2. Protein adsorption

Proteins used were γ-globulin(F-II)(IgG), bovine serum albumin(F-V)(BSA), and lysozyme(egg, 3Xcryst). They were labeled by ^{125}I using the Chloramine-T method[15]. Protein adsorption was conducted at 37°C in phosphate buffered saline(PBS) of pH 7.4 for the prescribed time. After adsorption, the polymer sample was rinsed with 60ml of PBS and the amount of adsorbed proteins was determined by the radioactivity measurement, using a gamma-ray scintillation counter. The sample size was always fixed to 10mm x 10mm x 0.5mm. The

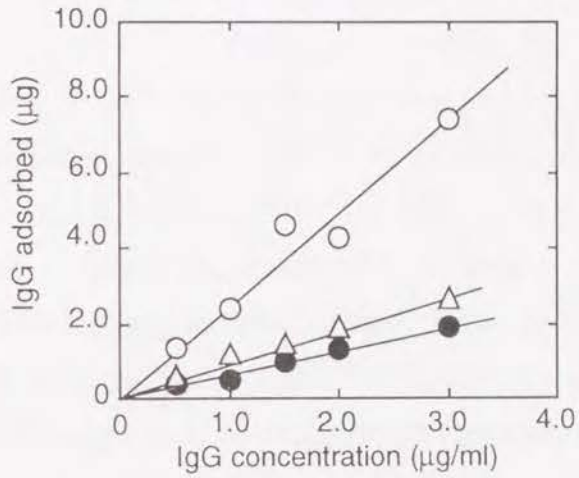

Figure 1. IgG adsorption on PVA and PHEMA hydrogels as a function of IgG concentration. (PVA hydrogel water content; 85 wt%)
(○) translucent PVA hydrogel ; (●) transparent PVA hydrogel
(△) PHEMA hydrogel

extent of adsorption was expressed by the absolute weight of adsorbed proteins in μg but not normalized to that per cm^2 of hydrogel surface, because exact estimation of the surface area of hydrogel sample was too difficult due to the porous structure of the PVA hydrogels.

RESULTS

1. Effect of protein concentration

Figure 1 shows the dependence of the amount of adsorbed IgG on the protein concentration in solution. The amount of adsorbed protein

linearly increases with the increasing IgG concentration for all the hydrogels. The transparent PVA hydrogel shows lower adsorption than the translucent hydrogel. For example, the amount of adsorbed IgG on the transparent PVA hydrogel at the IgG concentration of 1.0 mg/ml is 0.55μg, whereas that of translucent PVA hydrogel is 2.64μg. Therefore, the protein amount adsorbed on the translucent PVA hydrogel is 5 times as high as that of transparent PVA hydrogel. Furthermore, the IgG amount on the transparent PVA hydrogel is lower than on PHEMA which has a water content half of that of transparent PVA hydrogel. Figure 2 shows the result of BSA adsorption. As is seen, BSA adsorption shows the same tendency as that of IgG. When the amount of adsorbed IgG and BSA is compared at the same protein concentration, the translucent PVA and the PHEMA hydrogel exhibit higher BSA adsorption, while the transparent PVA hydrogel is much lower in the BSA adsorption. This suggests that the transparent PVA hydrogel shows adsorption behavior different from the translucent and PHEMA hydrogels. The result of lysozyme adsorption is shown in Figure 3. The dependence of lysozyme concentration is the same as that of IgG and BSA. The amount of adsorbed lysozyme is the smallest for the transparent PVA hydrogel, being 1/3 and 1/2 of that of translucent PVA hydrogel and PHEMA hydrogel, respectively. It is well known that lysozyme has a biodefence function by hydrolyzing polysaccharides in the bacterial cell wall and is first adsorbed on contact lenses among the tear proteins. As described above, a major cause for clouding of worn contact lens is protein adsorption. If protein adsorption is one of the serious problems for the long term wearing of contact lenses, the transparent PVA hydrogel may be a promising material for long-term

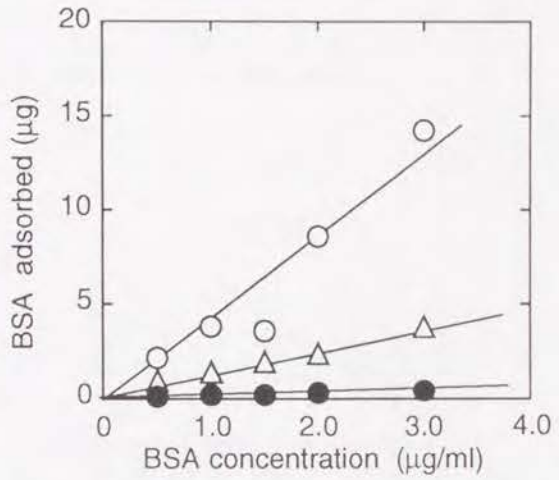

Figure 2. BSA adsorption on PVA and PHEMA hydrogels as a function of BSA concentration. (PVA hydrogel water content; 85 wt%)
(○) translucent PVA hydrogel ; (●) transparent PVA hydrogel
(△) PHEMA hydrogel

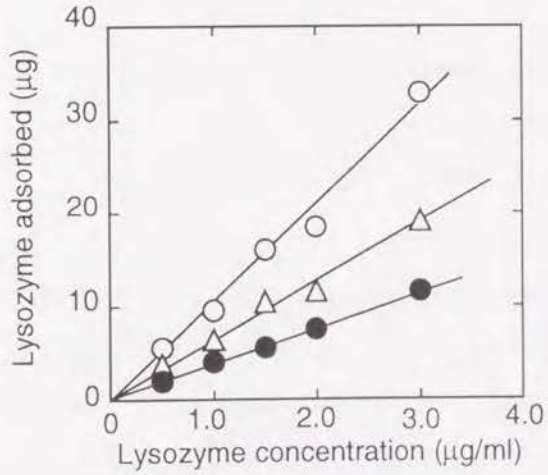

Figure 3. Lysozyme adsorption on PVA and PHEMA hydrogels as a function of lysozyme concentration.
(PVA hydrogel water content; 85 wt%)
(○) translucent PVA hydrogel ; (●) transparent PVA hydrogel
(△) PHEMA hydrogel

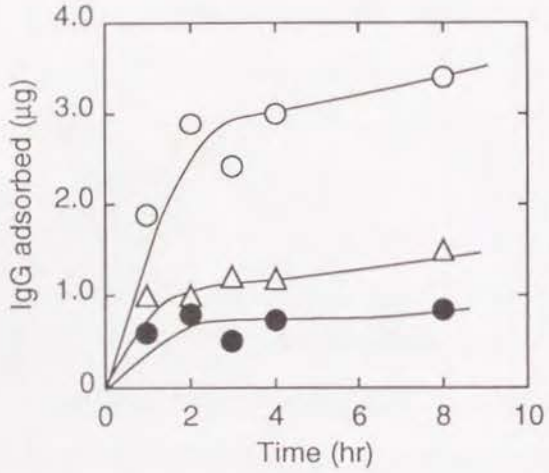

Figure 4. Time dependence of IgG adsorption on PVA and PHEMA hydrogels. (PVA hydrogel water content; 85wt%)
(○) translucent PVA hydrogel ; (●) transparent PVA hydrogel
(△) PHEMA hydrogel

wearing, as its lysozyme adsorption is less than that of the conventional soft contact lens materials.

2. Effect of adsorption time

The amount of adsorbed IgG is plotted as a function of adsorption time in Figure 4. The IgG concentration is 1.0 mg/ml. For all the hydrogels, adsorption steeply increases up to 3 hr and then slows down. Again, the highest adsorption is observed on the translucent PVA hydrogel while the lowest is on the transparent PVA hydrogel. Figures 5 and 6 present the results of BSA and lysozyme adsorption at the BSA and lysozyme concentration of 3.0 and 1.5 mg/ml, respectively. Apparently, BSA and lysozyme show an adsorption tendency similar to IgG.

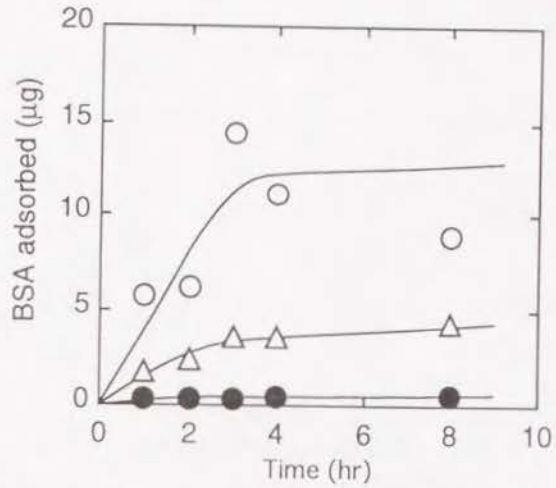

Figure 5. Time dependence of BSA adsorption on PVA and PHEMA hydrogels. (PVA hydrogel water content; 85 wt%)
(○) translucent PVA hydrogel ; (●) transparent PVA hydrogel
(△) PHEMA hydrogel

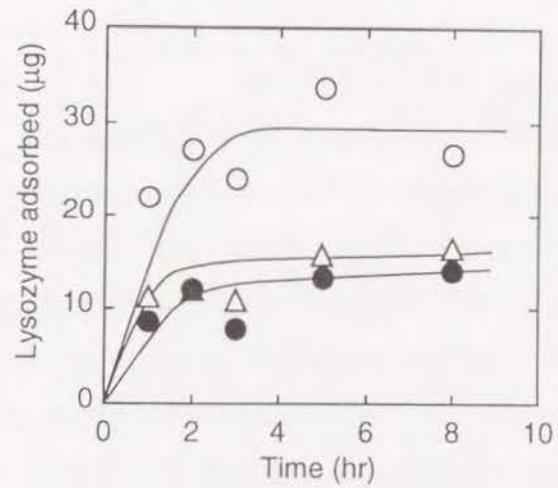

Figure 6. Time dependence of lysozyme adsorption on PVA and PHEMA hydrogels. (PVA hydrogel water content; 85 wt%
(○) translucent PVA hydrogel ; (●) transparent PVA hydrogel
(△) PHEMA hydrogel

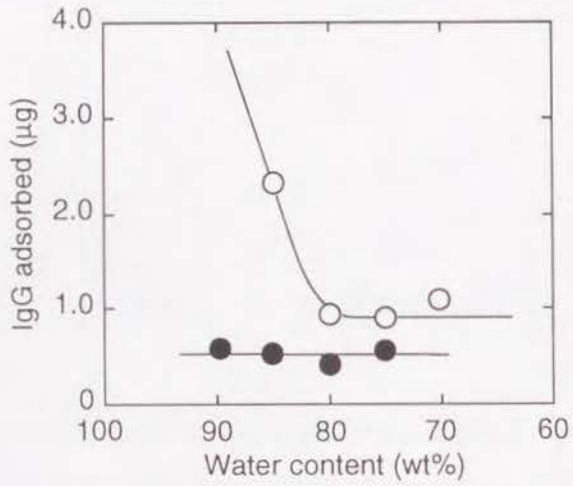

Figure 7. IgG adsorption on PVA hydrogels as a function of their water content.
(○) translucent PVA hydrogel ; (●) transparent PVA hydrogel

3. Effect of water content of PVA hydrogel

The effect of the water content of PVA hydrogel on adsorption of IgG after 3 hr is shown in Figure 7. The IgG concentration is 1.0 mg/ml. The water content of PVA hydrogel was varied by the PVA concentration of PVA solution at gel formation. As is seen from Figure 7, IgG adsorption on the translucent PVA hydrogel depends on the water content of hydrogel. The adsorption drastically decreases up to 80 wt% and then remains constant. In contrast, in the case of transparent PVA hydrogel, the IgG adsorption is independent of the water content of hydrogel at least between 75 and 80 wt%. For the PVA hydrogel with the water content of 85 wt%, IgG adsorption on the translucent PVA hydrogel is 5 times as large as that of transparent PVA hydrogel. In

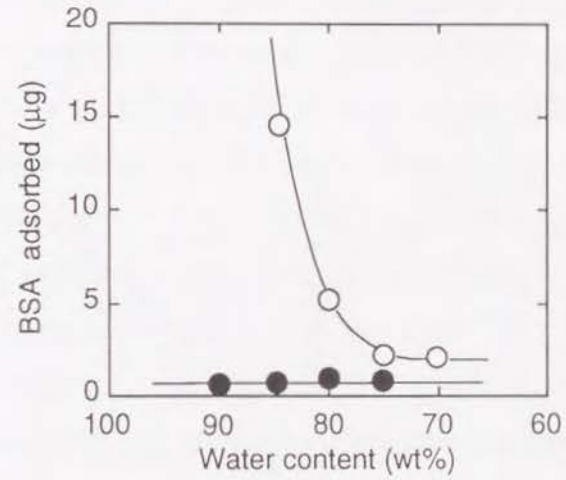

Figure 8. BSA adsorption on PVA hydrogels as a function of their water content.
(○) translucent PVA hydrogel ; (●) transparent PVA hydrogel

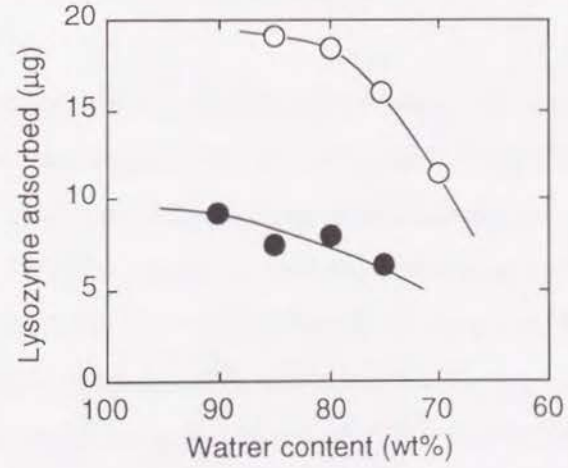

Figure 9. Lysozyme adsorption on PVA hydrogels as a function of their water content.
(○) translucent PVA hydrogel ; (●) transparent PVA hydrogel

contrast, difference in amount of adsorbed IgG between the transparent and the translucent PVA hydrogel becomes smaller, when the water content of hydrogel is below 80 wt%. This tendency is seen more clearly for BSA as shown in Figure 8. Figure 9 shows the result of lysozyme absorption at a protein concentration of 1.5 mg/ml. The lysozyme adsorption is different from that of IgG and BSA. The amount of adsorbed IgG and BSA depends on the water content of hydrogel for the translucent PVA hydrogel but not for the transparent PVA hydrogel. However, lysozyme adsorption depends on the gel water content even for the transparent PVA hydrogel, although the amount of adsorbed lysozyme on the transparent PVA hydrogel is much smaller than that of the translucent PVA hydrogel, which shows drastic decrease of lysozyme adsorption with the decreasing water content.

DISCUSSION

As described above, the behavior of protein adsorption onto the PVA hydrogel prepared by low temperature crystallization is greatly different between the translucent and the transparent hydrogel. This difference seems to be related to the structure of PVA hydrogels. As disclosed in Chapter 1 and 2, the translucent PVA hydrogel is porous and the pore size decreases with the decreasing water content. In contrast, the transparent PVA hydrogel has almost smooth surface structure or porous structure with the pore size below 1μm, independent of the water content.

It is reported that smooth PVA film without heat treatment hardly adsorbs protein[17]. Referring to this fact, the protein adsorption observed

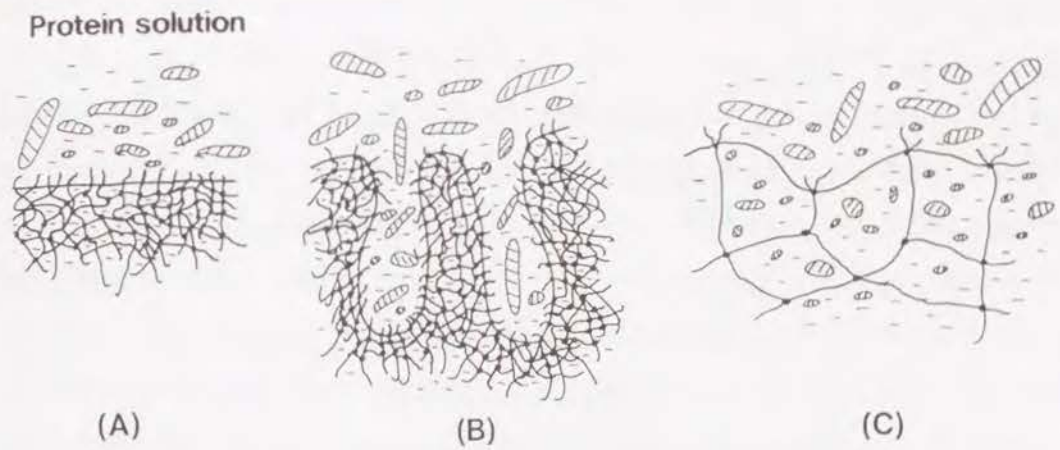

Figure 10. Schematic presentation of gel/protein solution interface for an ideal PVA hydrogel (A) and porous PVA hydrogels(B and C).

on the PVA hydrogels can be interpreted as follows. Protein may be adsorbed on the hydrogels in two manners as depicted in Figure 10. One is trapping in pores of the PVA hydrogel surface region as shown in Figure 10 (B) and the other is penetration into the hydrogel network structure as in Figure 10 (C). The protein trapping must strongly depend on the surface porous structure while the protein penetration should depend on the molecular weight of protein. If an ideal PVA hydrogel having such a structure as shown in Figure 10 (A) is subjected to protein adsorption, protein may be hardly adsorbed on the hydrogel similar to the PVA film without heat treatment. However, the translucent PVA hydrogel with porous structure may undergo both protein trapping

and protein penetration. For high water content PVA hydrogels with a large pore size protein may be trapped easily in pores of the PVA hydrogel surface region, so that significant adsorption may take place. In contrast, for low water content PVA hydrogels with a small pore size protein cannot be readily trapped in pores of the PVA hydrogel surface. This explanation is supported by the fact that the higher the water content and the lower the molecular weight of protein the adsorption was enhanced. On the contrary, the transparent PVA hydrogel with less clear porous surface structure hardly underwent the protein trapping. IgG and BSA could not penetrate into the transparent PVA hydrogel probably because of their relatively high molecular weights. Consequently, protein adsorption on the transparent PVA hydrogel is virtually independent of the water content, leading to low adsorption. However, lysozyme which has smaller molecular weight(14,600) than IgG and BSA, may easily penetrate even into the transparent PVA hydrogel. As a result, a large amount of lysozyme will be adsorbed, be depending on the water content of PVA hydrogel.

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CHAPTER 7

Poly(vinyl alcohol) hydrogel as soft contact lens materials

INTRODUCTION

Biomaterials widely used as soft contact lenses include silicone elastomer[1], copolymer[2] of butyl acrylate(BA) and butyl methacrylate (BMA) as hydrophobic lens and poly(2–hydroxyethyl methacrylate) (PHEMA)[3] and copolymer[4] of methyl methacrylate(MMA) and vinyl pyrrolidone(VP) as hydrophilic lens. These soft contact lens materials present usually higher oxygen permeability than hard contact lens materials, but the hydrophobic materials have disadvantages such as poor wear feeling caused by low water wettability, remarkable adsorption of lipids. On the other hand, the hydrophilic materials give rise to significant protein adsorption and are very low in mechanical strength, although they give excellent wear feeling and minimum damage to the cornea.

PVA hydrogel has already been proposed as a material for soft contact lens, for instance, by crosslinking with glyoxal or borate[5]. Furthermore, preparation of a PVA soft contact lens though annealing[6] is proposed, but this needs a long and complicated fabrication process, although it has a high water content and high mechanical strength.

In Chapter 2 it reported that the transparent PVA hydrogel could be obtained from new preparation method of PVA hydrogel, which involves dissolution of PVA in a mixed solvent consisting of water/organic solvent and the subsequent crystallization of PVA at a

low, but not extraordinarily low, temperature.

This Chapter was undertaken in an attempt to explore the possibility of using the PVA hydrogel with high water content and high mechanical strength as soft contact lens.

EXPERIMENTAL

1. PVA hydrogel membrane

1-1. Preparation

Commercial PVA with a degree of saponification of 99.5 mol% and a viscosity-average degree of polymerization of 1,700 was used to prepare PVA solution with various PVA concentrations. PVA solution was obtained by heating a mixture of PVA powder and a mixed water/dimethyl sulfoxide(DMSO) solvent at 120°C. Following cooling the PVA solution to about 60°C, it was cast on a glass plate and then allowed to stand at -20°C for 24 hr to achieve PVA crystallization. The resulting PVA gel was immersed in water at room temperature for 3 days and then air-dried overnight. Following drying the gel further under vacuum overnight to remove the organic solvent remaining in the gel, it was again put in water for hydration at 37°C for 2 days. The water content of the hydrated PVA gel was calculated from the equation:

$$\text{Water content}(\%) = \frac{W_h - W_d}{W_h} \times 100$$

where W_h is the weight of hydrated PVA hydrogel and W_d is the weight

of dried PVA hydrogel.

1-2. Physical properties

Tensile strength and elongation at break were measured on the PVA membranes at 25°C under a tensile speed of 50 mm/min using Autograph S-100 of Shimadzu Inc., Kyoto, Japan, and five measurements were averaged. The membrane samples were cut to dumb-bell test pieces in accordance with JIS specifications.

Light transmittance at 550nm was measured for the PVA gels of 0.5mm thickness under immersion in water at 25°C. Oxygen permeability of the hydrogel membranes was measured at 35°C using a conventional gas permeation apparatus to be applied for polymer films[7].

Protein adsorption was conducted at 37°C using γ-globulin(IgG), bovine serum albumin(BSA), and lysozyme. Labeling of proteins with ^{125}I was performed with the Chloramine-T method[8]. Protein adsorption was conducted at 37°C in phosphate buffered saline(PBS) of pH 7.4 for 3hr. After allowing the adsorption, the SCL was rinsed with 60ml of PBS and amount of adsorbed protein was measured with the radioactivity, which used gamma-ray scintillation counter.

2. PVA hydrogel soft contact lens

2-1. Preparation

A mixed solvent of water/DMSO(20/80, w/w) was added to PVA powder so as to have a PVA concentration of 20 wt%. The PVA solution was prepared by heating the mixture for 2 hr at 120°C. Following cooling the PVA solution to 50~60°C, it was poured into a mold. The one surface of the mold was virtually spherical and convex, while the

other was spherical and concave. The distance between the central part of the convex and the concave surface was 0.2mm. The PVA solution in the mold was allowed to stand for 1 hr in a refrigerator kept at −20°C to effect crystallization of PVA. The resulting PVA gel lens was removed from the mold and the organic solvent in the gel lens was exchanged with water by immersing the gel in water for 3 days at room temperature. The base curve and diameter of PVA contact lens were 8.0 and 14mm, respectively.

2−2. Animal tests

The PVA hydrogel contact lens was applied to albino rabbit eyes continuously for a period of 3 months. After PVA hydrogel contact lens was worn to the rabbit eyes, one−thirds on nose part of rabbit eyelid was sutured. Slit−lamp biomicroscopic examination was performed after extended wear for 12 weeks. For each examination, light microscopy was carried out following enucleation of the eyes, which were fixed in 20 wt% formaldehyde and stained with hematoxylin and eosin(HE). At the 12th week after application of the lens, the enucleated eyes were fixed in 2.5 wt% glutaraldehyde and then processed for scanning electron microscopy(SEM) using the standard technique. The central cornea thickness was evaluated in vivo using an ultrasonic pachymeter. The measurement was made before insertion of the contact lens and 1, 2, 3, 4, 5, and 6 weeks thereafter. Four readings were made for each eye, and the mean values were recorded and compared with those from the rabbits without PVA lens.

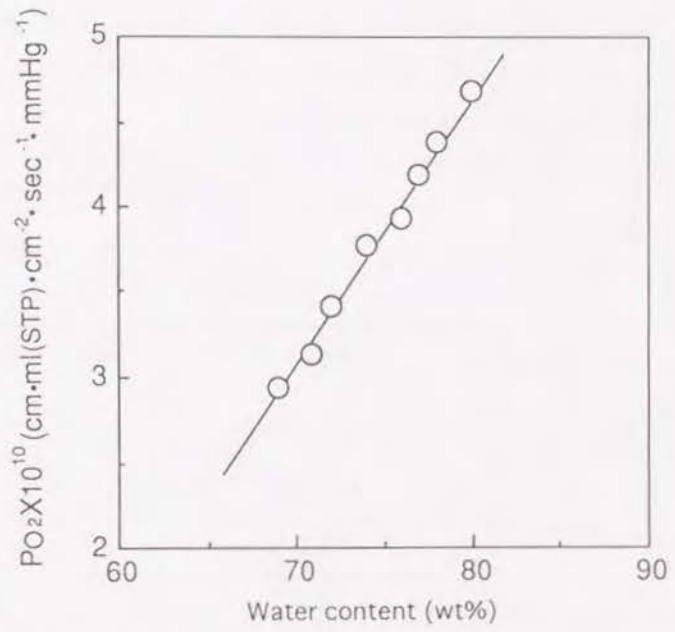

Figure 1. Effect of the water content on the oxygen permeability coefficient of PVA hydrogels at 35°C.

RESULTS

1. In vitro evaluation

The oxygen permeability of PVA hydrogel with different water contents is shown in Figure 1. It is seen that the oxygen permeability depends greatly on the water content of PVA hydrogels.

Table 1 compares physical properties of PVA hydrogel membrane with those of PHEMA and MMA/VP copolymer which are currently being applied clinically as soft contact lenses. In general, the strength of hydrogel will vary inversely with the water content.

Table 1. Comparison of physical properties of PVA hydrogel with other contact lens materials.

	PVA	MMA/VP copolymer (Breath–O^R)	PHEMA (Hydron^R)
Water content, wt%	78	78	38
Tensile strength, kg/cm^2	47	19	10
Elongation, %	500	160	160
Light transmittance, %[a)]	99–100	99–100	99–100
O_2 permeability [b)]	4.4	4.6	1.0

a) 550nm, 0.2mm thick, in water
b) 10^{-10}· cm^3(STP)·cm/cm^2·sec·mmHg (35°C)

However, as Table 1 indicates, PHEMA has relatively low strength although it has a water content as low as 38 wt%. The MMA/VP copolymer is superior in terms of water content, but has only marginally greater strength. On the contrary, the PVA hydrogel membrane has a tensile strength approaching 50 kg/cm^2, five times stronger than PHEMA, although the water content is as high as 78 wt%. The mechanical properties of PVA membrane could be further improved by irradiation in a deaerated atmosphere with high energy radiation[8]. Oxygen permeability increases simply with the water content, indicating that the oxygen permeabilities of both MMA/VP copolymer and PVA are superior to that of PHEMA.

Table 2. Protein adsorption to PVA and conventional soft contact lenses. (n=4)

Lens	Water content(wt%)	IgG (μg/cm^2)	BSA (μg/cm^2)	Lysozyme (μg/cm^2)
PVA	78	0.074±0.006	0.005±0.001	0.195±0.014
MMA/VP copolymer (Breath–O^R)	78	0.889±0.011	0.169±0.021	4.991±0.165
PHEMA (Hydron^R)	38	0.271±0.013	0.037±0.004	0.230±0.016

To study protein adsorption to the PVA hydrogel contact lens, protein adsorption on the PVA soft contact lens measured for three proteins, serum albumin, γ–globulin, and lysozyme. In Chapter 6, the amount of proteins adsorbed to the PVA hydrogel increased with the increasing concentration of protein in solutions. Therefore protein adsorption was conducted at the concentration of 1.0, 3.0, and 1.5 mg/ml for IgG, BSA, and lysozyme, respectively. Table 2 gives the results, together with those of commercially available soft contact lenses. Clearly, the PVA hydrogel contact lens exhibits very low protein adsorption, whereas protein adsorption to the MMA/VP copolymer is 10 to 40 times as high as that of the PVA contact lens. It may be expected that our PVA hydrogel contact lens will remain relatively stable and resistant to protein staining over a prolonged period of time.

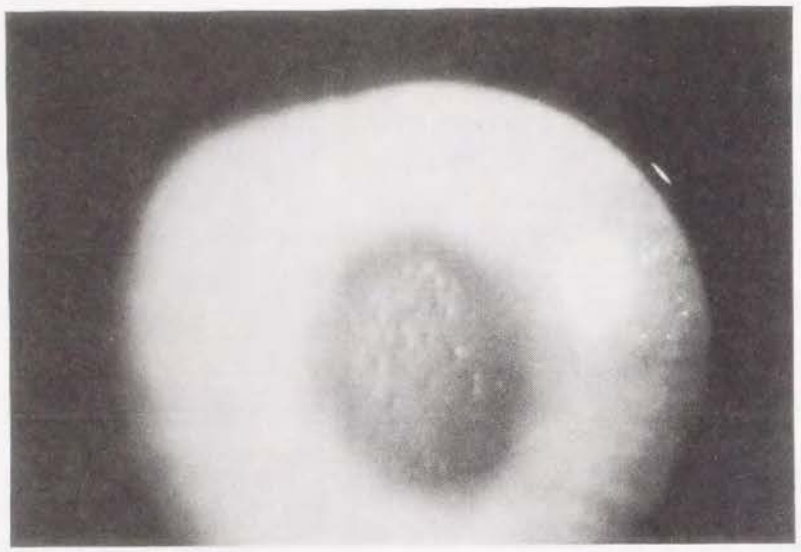

Figure 2. Slit lamp microscopic photograph of rabbit eye after extended wear of PVA hydrogel contact lens for 3 weeks.

2. In vivo evaluation

Many studies have shown that corneal edema results from the overnight wear of rigid contact lenses by human subjects[13-17]. Figure 2 shows a slit-lamp microscopic photograph of rabbit eye on which the PVA hydrogel contact lens resided for 3 weeks. This slit-lamp biomicroscopic examination reveals no abnormal findings such as conjunctival hyperemia, cornea edema, cornea neovascularization, and lens pollution during the experimental period. It have usually noticed that the ultrastructural changes of cornea were related to the wearing duration and the oxygen transmissibility of contact lens worn[18-21]. Table 3 shows the thickness of cornea which wore the PVA hydrogel contact lens continuously for a period of 3 months, together with that of non-

Table 3. Change in central cornea thickness[a)] of rabbit eyes after extended wear of PVA lens

	Wearing days								
	Initial	1	3	7	14	21	28	35	42
wearing eye (n=4)	374 (μm)	377	376	374	374	378	373	372	376
non-wearing eye (n=4)	373 (μm)	373	376	372	373	373	–	–	–

a) measured with ultrasonic pachymeter 200 and expressed in μm unit

wearing eyes. Normal cornea thickness is about 370μm. No difference in cornea thickness was noted between the non-wearing and the wearing eyes. The histological section of the rabbits cornea after extended wear for 3, 6 and 9 weeks are shown in Figure 3. This histological study again shows no difference in thickness of the cornea epithelium and cell arrangement between the non-wearing and the wearing eyes. SEM photographs of the cornea epithelium of the eyes which wore the PVA contact lens are given in Figure 4. As is evident, the cornea epithelium of the eyes which wore the PVA lens for 12 weeks shows no abnormal tissue and no difference between the wearing and the non-wearing eye.

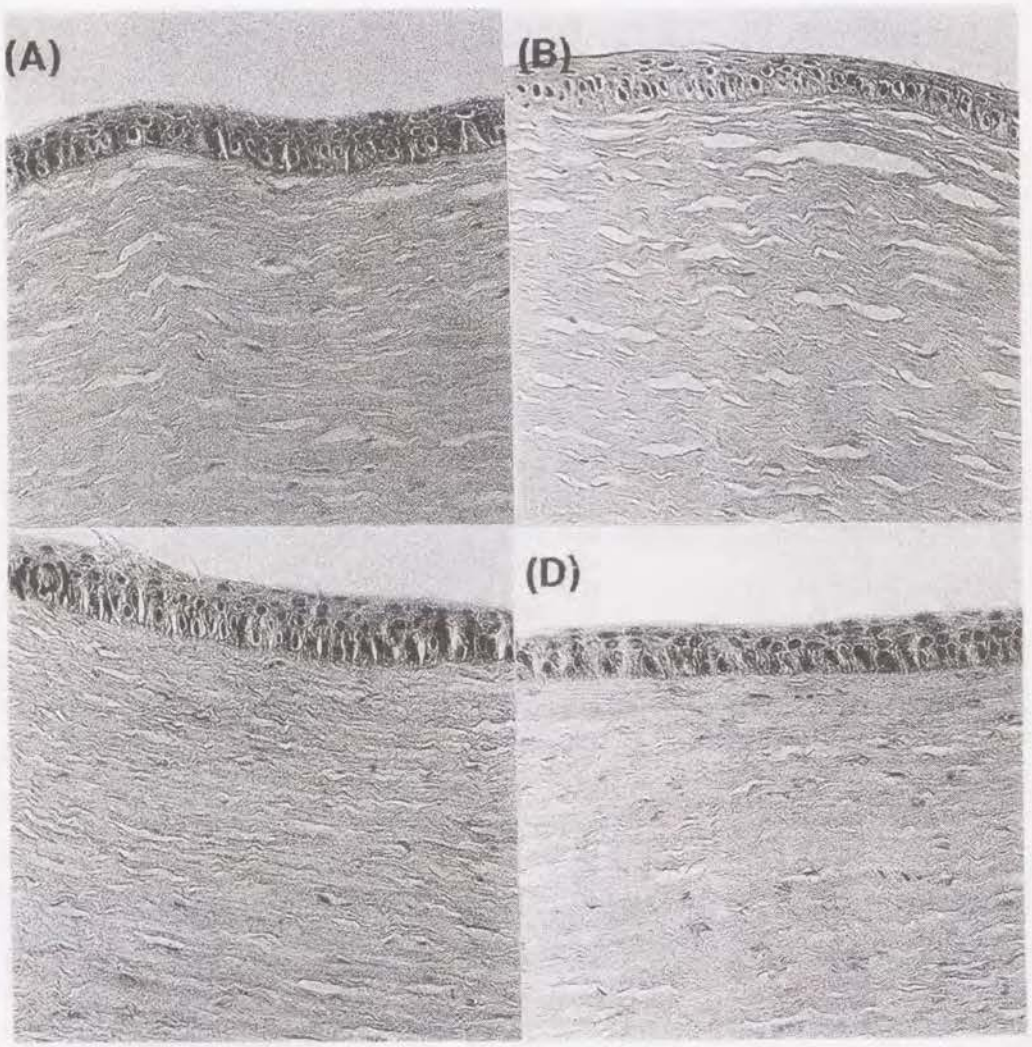

Figure 3. Histological section of rabbit cornea stained with HE after extended wear of PVA hydrogel contact lens.
(A) control
(B) 3 weeks wear
(C) 6 weeks wear
(D) 9 weeks wear

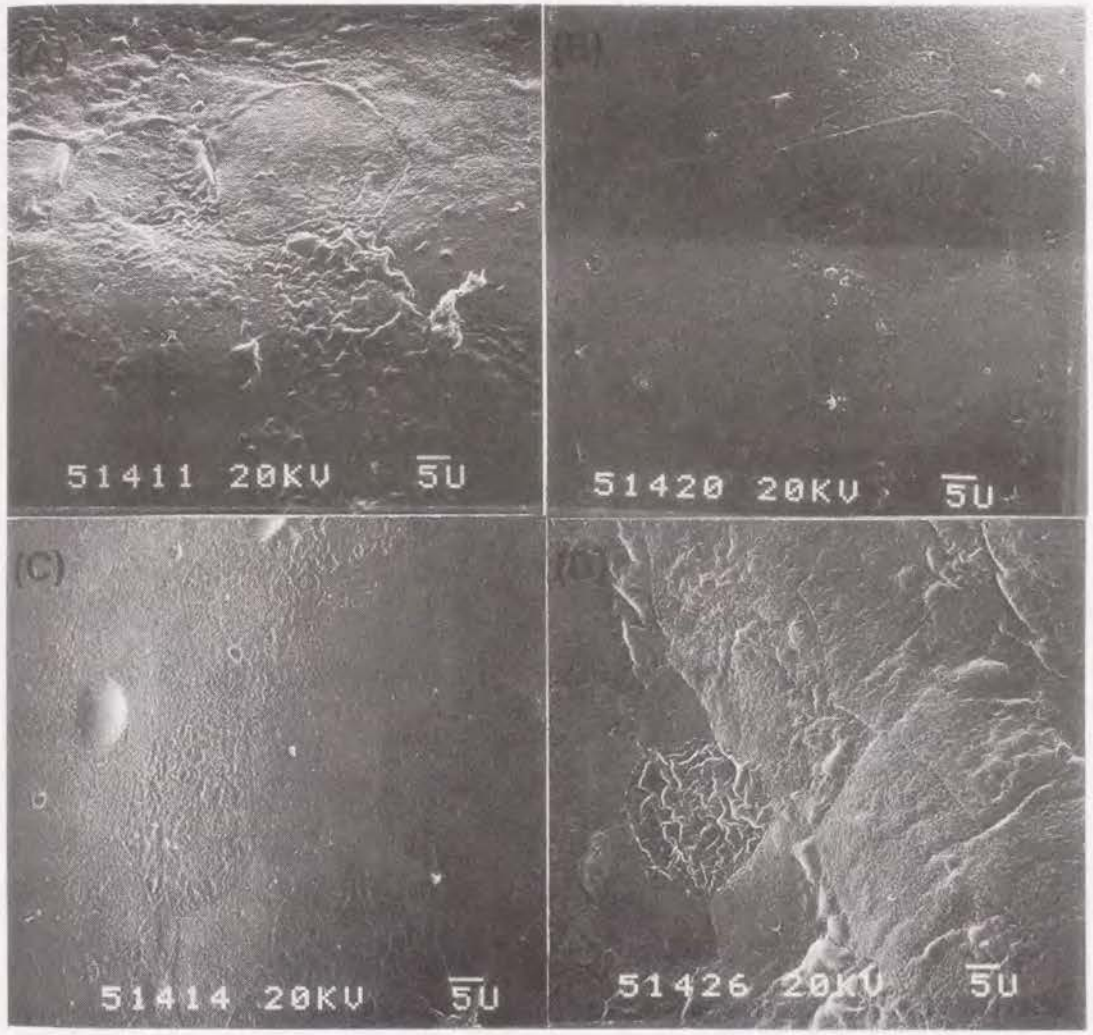

Figure 4. SEM photographs of rabbit cornea epithelium after extended wear of PVA hydrogel contact lens.
(A) control
(B) 6 weeks wear
(C) 9 weeks wear
(D) 12 weeks wear

DISCUSSION

For the preparation of PVA hydrogel there have been reported a number of methods which do not use any additives while keeping the gel water content high[9-11]. However, all of the PVA hydrogels prepared are optically opaque or translucent to be used as the contact lens material. On the contrary, PVA hydrogel prepared by dissolving PVA in a mixed solvent consisting of water and DMSO, followed by low temperature crystallization of concentrated PVA solution, is optically clear. This transparent hydrogel contains neither additives nor chemical cross-linking agents, but retains the water-swollen state through microcrystalline domains formed by hydrogen bonding between the hydroxyl groups of PVA chains.

The water content of the newly developed PVA hydrogel contact lens is 78±1 wt%, which is the same as cornea, and the gel tensile strength is 50 kg/cm^2 which is about 3 times as high as that of a commercially available soft contact lens. The PVA contact lens may be used for long-term wear because of its high oxygen permeability. Moreover, the lysozyme adsorption test revealed that the protein adsorbed to the PVA lens was in the level of 0.2 μg/cm^2, which is 1/2 to 1/30 of that of conventional soft contact lenses. The animal test showed no abnormality after continuous wear for 12 weeks. From these result the newly developed transparent PVA hydrogel indicate good soft contact lens material which is possible for the continuous long-term wear.

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CHAPTER 8

Gel spinning of poly(vinyl alcohol)

INTRODUCTION

Many attempts have been made to develop high strength and high modulus fibers from conventional polymers such as polyethylene (PE)[1-6], polypropylene(PP)[7-9], polyoxymethylene(POM)[10,11], and poly(vinyl alcohol)(PVA)[12-19]. Among these non-rigid polymers, PP and POM have been found to produce fibers with relatively low moduli because the theoretically attainable modulus is low due to their inherent spiral chain structure. On the contrary, PE and PVA have potentiality to yield high strength and high modulus fiber, since they have high theoretically attainable moduli because of their planar zig-zag structure. As PVA has a melting temperature as high as 230°C in contrast to PE with a low melting temperature such as 130°C, it seems possible that high strength and high modulus fibers comparable to Aramid can be fabricated from PVA.

PVA fibers produced by wet spinning from aqueous solution have been widely used in industry, but are quite low both in strength and modulus in comparison with Aramid fibers. Therefore, to enhance the strength and modulus, organic solutions have been proposed as spinning dope instead of aqueous solutions. They include: (1) glycerin(GC), ethylene glycol(EG), or ethyleneurea solutions, from which dry spinning was carried out[15]; (2) dimethyl sulfoxide(DMSO) solution, which was used for wet-spinning into organic non-solvents such as methanol,

ethanol, benzene, and chloroform[16]; (3) DMSO solution, from which dry–wet spinning was performed, followed by 20 times drawing of the undrawn fibers[17]; and (4) 2–15 wt% GC and EG solutions, which were employed as the dope for gel spinning of PVA with the molecular weight higher than 500,000[18,19]. However, the fibers obtained from these dopes exhibit in all cases strength lower than 20 g/d(2.4 GPa) and modulus lower than 500 g/d(60 GPa), which are far inferior to those of Aramid fibers.

The key factor for fabrication of high strength and high modulus fibers from such non–rigid polymers is how to extend and orient the folded polymer chains along the fiber axis to a very high degree. Smith and Lemstra have succeeded in producing PE fibers having strength and modulus higher than 3.0 and 100 GPa, respectively, by gel spinning of high molecular weight PE[1,2]. The gel spinning made it possible to draw the PE fiber to high ratios under formation of high strength and high modulus fibers. In Chapter 2, it have found that a high water content and high strength transparent PVA hydrogel with approximately 2 times higher strength and 1.5 times higher elongation than that of conventional PVA hydrogel could be obtained from PVA solution prepared from mixed solvents consisting of water and a water–miscible organic solvent such as DMSO.

This Chapter will describe gel spinning of PVA from spinning dope consisting of H_2O/DMSO mixture to produce highly drawable PVA fibers.

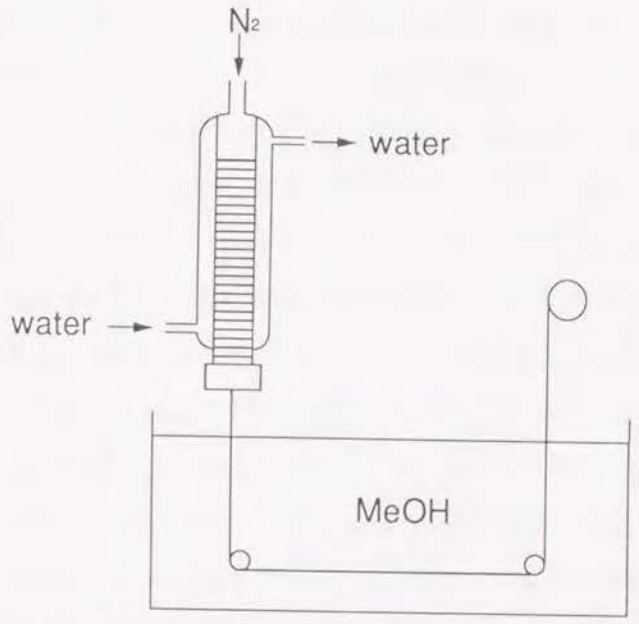

Figure 1. Apparatus of dry–wet spinning process.

EXPERIMENTAL

1. Gel spinning

PVA powders were kindly supplied by Unitika Co.,Ltd, Osaka, Japan. The PVA used has viscosity–average degrees of polymerization(DP) of 1,700 and 5,000, both, with a degree of saponification of 99.5 mol%. Unless otherwise specified, PVA with DP of 5,000 was used throughout this work. The PVA spinning dope was prepared from H_2O/DMSO mixtures and homogenized at 140°C in nitrogen atmosphere to prevent PVA from oxidative degradation. Dry–wet spinning was performed by extruding the dope from a nozzle having a hole size of 0.6mm. The dope was first extruded into open air at 30 to 60°C, and then immediately coagulated in methanol kept at various

temperatures to obtain undrawn PVA gel fibers. The arrangement of spinning apparatus is depicted in Figure 1. Coagulating temperatures below room temperature were achieved using a cooler immersed in methanol. The temperature of coagulation bath could be controlled within ±1°C. Unless otherwise specified, the PVA concentration of spinning dope was 6 wt% and the temperature of coagulation was −20°C. The dried fibers were drawn to various degrees in a silicone oil bath kept at various temperatures. Unless otherwise specified, two−stage drawing was carried out first at 160°C and second at 200°C.

2. Physical measurements

2−1. Tensile properties

Tensile properties of the undrawn dried fibers were measured at a cross−head speed of 10 mm/min, a gauge of 10mm, 25°C, and a relative humidity of 65%. The tensile strength and Young's modulus of the drawn fibers were measured at a cross−head speed of 20 mm/min, a gauge length of 50mm, 25°C, and a relative humidity of 65%. Autograph S−100, manufactured by Shimadzu Inc., Kyoto, Japan, was used for these tensile measurements. The Young's modulus of PVA fibers was calculated from the initial slope of stress−strain curve. All the tensile properties presented here are based on the initial diameter of fiber which was determined by microscope. The tensile strength and modulus of fiber was measured on five samples and averaged.

2−2. Fiber density

The density of PVA fibers was measured with a density gradient column using mixtures of benzene and carbon tetrachloride at 30°C. The

crystallinity of PVA fibers was calculated from their density using the following equation:

$$1/\rho = X/\rho_c + (1-X)/\rho_a \qquad (1)$$

where ρ_c is the density of PVA crystalline part(1.345 g/cm^3), ρ_a is the density of amorphous part(1.269 g/cm^3), and X is the crystallinity of PVA fiber[20].

2−3. X−ray diffraction and scanning electron microscopy

The X−ray diffraction pattern of fibers was taken with a flat film camera using Ni−filtered Cu−Kα with a Ru−300 X−ray diffraction apparatus of Rigakudenki Co.Ltd., Tokyo, Japan. The surface of PVA fibers was examined with a scanning electron microscope(SEM), Hitachi microscope S−450, after coating the samples with gold.

2−4. Differential scanning calorimetry

The thermal analysis of PVA film and fiber was performed by differential scanning calorimetry(DSC) with an apparatus manufactured by Shimadzu Inc., Kyoto, Japan, which was operated at a scan speed of 10 °C/min. The crystallinity of PVA fiber was calculated from the endothermic thermogram area of DSC assuming that the fusion enthalpy of 100% crystalline PVA is 37.3 cal/g[21]. Tin(Tm=232°C and ΔH=14.2 cal/g) was used as a standard of DSC measurement.

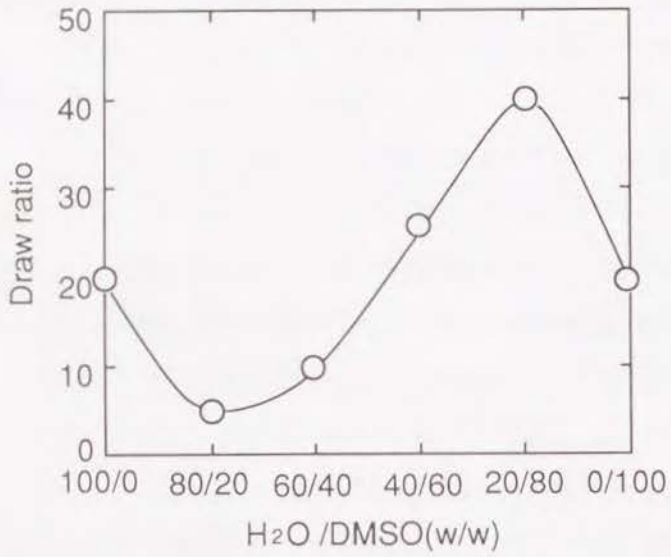

Figure 2. The effect of H_2O/DMSO mixing ratio in spinning dope on the draw ratio of PVA fibers spun from 20 wt% PVA dope into methanol kept at −20°C. (DP=1,700)

RESULTS

1. Effect of H_2O/DMSO ratio in mixed solvent

In Chapter 2, it reported that high strength and high water content PVA hydrogel sheets can be prepared by low temperature crystallization of PVA solutions prepared from H_2O/DMSO mixed solvents. Figure 2 shows the effect of H_2O/DMSO ratio in the mixed solvent on the highest attainable draw ratio of spun fibers. The DP of PVA used is 1,700. It is noticed that the draw ratio *vs* the H_2O/DMSO ratio curve exhibits a minimum and a maximum. The PVA fiber spun from a H_2O/DMSO(20/80, w/w) mixture is found to have the highest draw ratio(40 times) when drawn twice at 160 and 200°C.

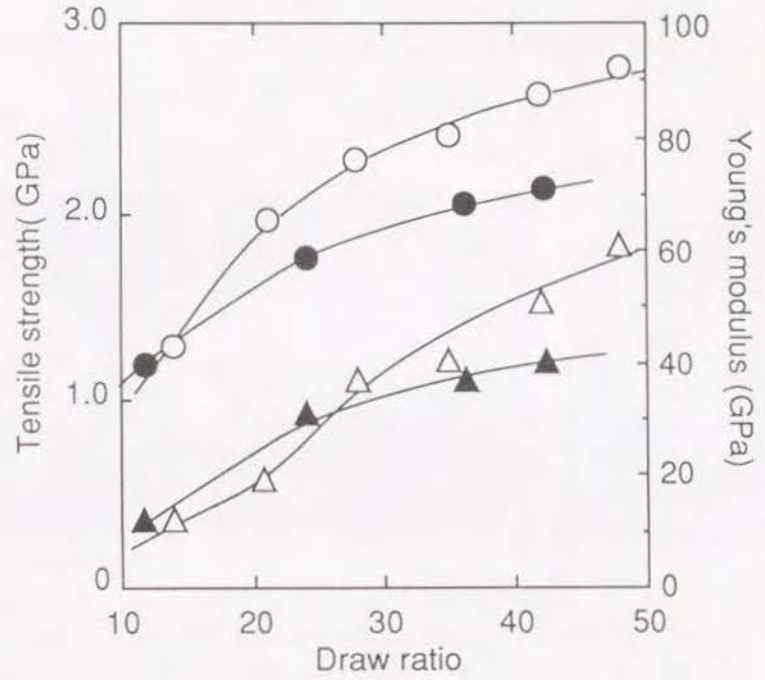

Figure 3. The tensile strength and Young's modulus of PVA fibers spun from 6 wt% PVA dope of different H_2O/DMSO mixtures into methanol kept at −20°C as a function of draw ratio.
(DP=5,000)
(○) Tensile strength ; (△) Young's modulus
Open marks ; 80 wt% DMSO Closed marks ; 100 wt% DMSO

Figure 3 represents the effect of draw ratio on the tensile strength and Young's modulus of PVA fiber, when the PVA concentration of spinning dope was 6 wt% and DP of PVA was 5,000. As is seen, the highest draw ratio which was attained for the PVA fiber from the H_2O/DMSO(20/80, w/w) mixture is 45 times and the tensile strength and the Young's modulus for the 45 times drawn PVA fiber are 2.8 and 64 GPa, respectively.

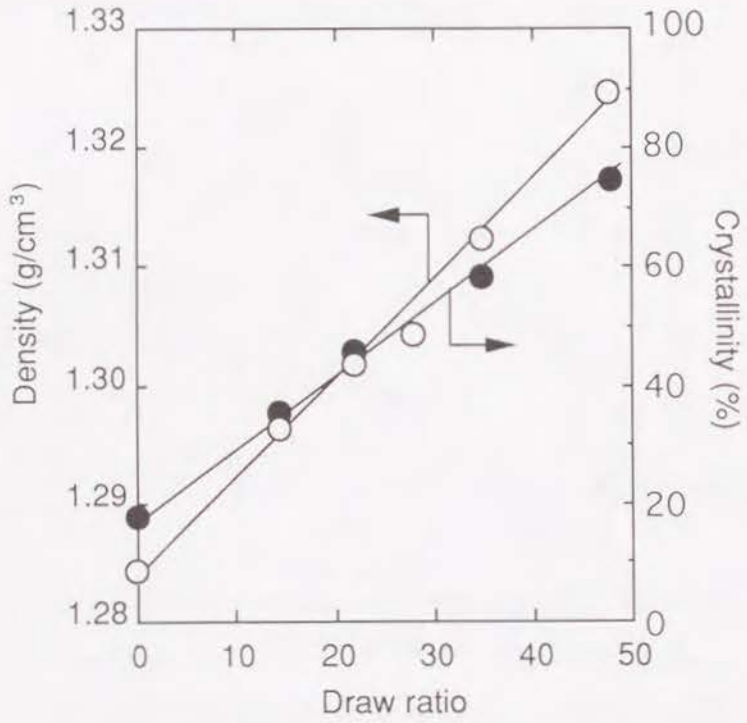

Figure 4. The density and crystallinity of PVA fibers spun from 6 wt% PVA dope of 80 wt% DMSO into methanol kept −20°C as a function of draw ratio. (DP=5,000)

The density of PVA fibers and the crystallinity estimated from it are shown in Figure 4 as a function of draw ratio. Both the density and the crystallinity of PVA fibers increase linearly with the increasing draw ratio, the 45 times drawn PVA fiber exhibiting the highest density of 1.325 and the highest crystallinity of 75%. Figure 5 shows wide-angle X-ray diffraction patterns of fibers undrawn and uniaxially drawn to 40 and 45 times ratios. Obviously, the pattern of undrawn fiber is composed of uniform circular rings, whereas the drawn fibers give a pattern characteristic of strongly oriented crystalline polymer.

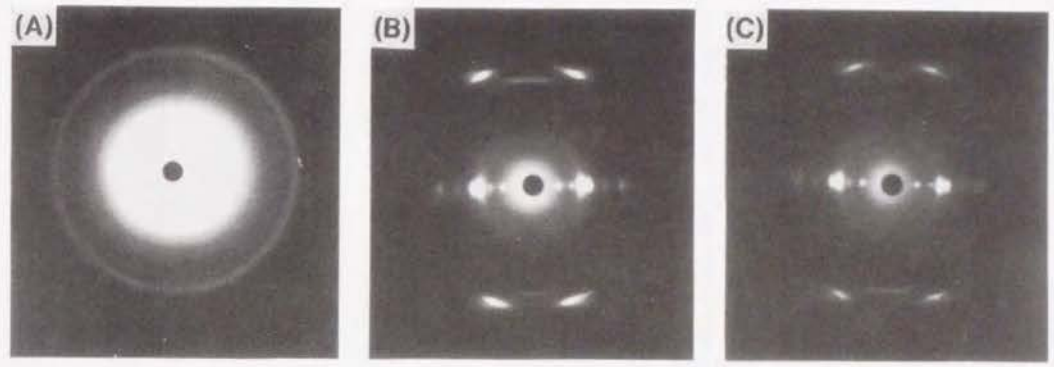

Figure 5. Wide-angle X-ray diffraction pattern of PVA fibers spun from PVA dope of 80 wt% DMSO into methanol kept at −20°C. (DP=5,000)
(A) undrawn ; (B) x40 ; (C) x45

2. Effect of coagulating temperature

The rate of PVA gelation occurring when the dope is extruded into cooled methanol must depend on the coagulating temperature and influence both the morphology of the undrawn fiber and the ultimate fiber properties. To study the effect of coagulating temperature on the fiber properties, 6 wt% PVA dope prepared from H_2O/DMSO(20/80) was spun into methanol kept from +20 to −20°C. When PVA fiber was coagulated at +18°C, phase separation of PVA fiber took place to give

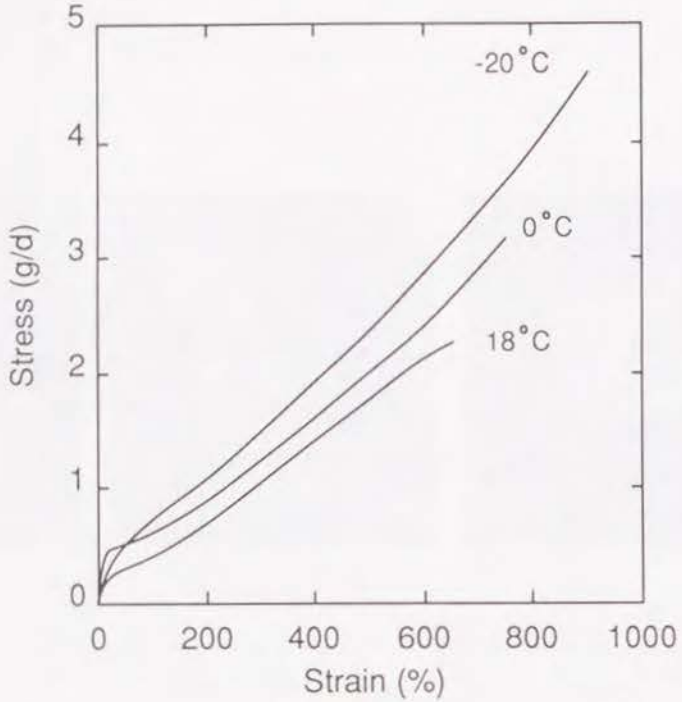

Figure 6. Typical stress–strain curves of undrawn PVA fibers spun from 6 wt% PVA dope of 80 wt% DMSO into methanol kept at different temperatures. (DP=5,000)

translucent appearance. In contrast, the PVA fiber coagulated at −20°C was transparent.

Typical stress–strain curves of the undrawn PVA fibers spun at various coagulating temperatures are shown in Figure 6. Both the stress and the strain of PVA fiber increase with the lowering coagulating temperature. For example, the elongation at break of the undrawn PVA fiber coagulated at +18°C is 650%, whereas coagulation at −20°C gives 950% elongation. Moreover, coagulation at −20°C yields an undrawn fiber with the tensile strength 2 times greater than that of the fiber coagulated at +18°C.

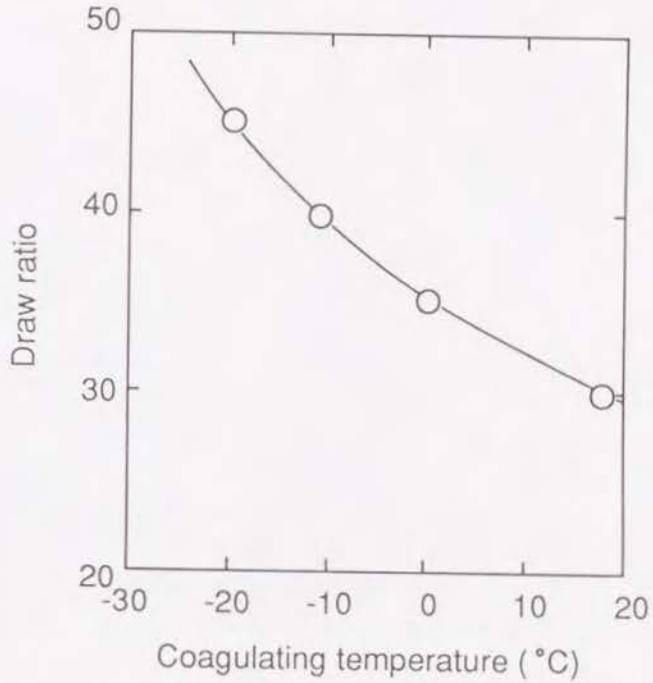

Figure 7. The highest attained draw ratio of PVA fibers spun from 6 wt% PVA dope of 80 wt% DMSO into methanol as a function of coagulating temperature. (DP=5,000)

Figure 7 represents the highest draw ratio attained for the dried PVA fibers which were coagulated at different temperatures. The 6 wt% PVA spinning dope was composed of H_2O/DMSO(20/80, w/w) and DP of PVA was 5,000. The total draw ratio is clearly affected by the coagulating temperature and exhibits the same tendency as for the stress–strain relation of undrawn PVA fibers. In other words, the highest draw ratio continuously increased with the lowering coagulating temperature.

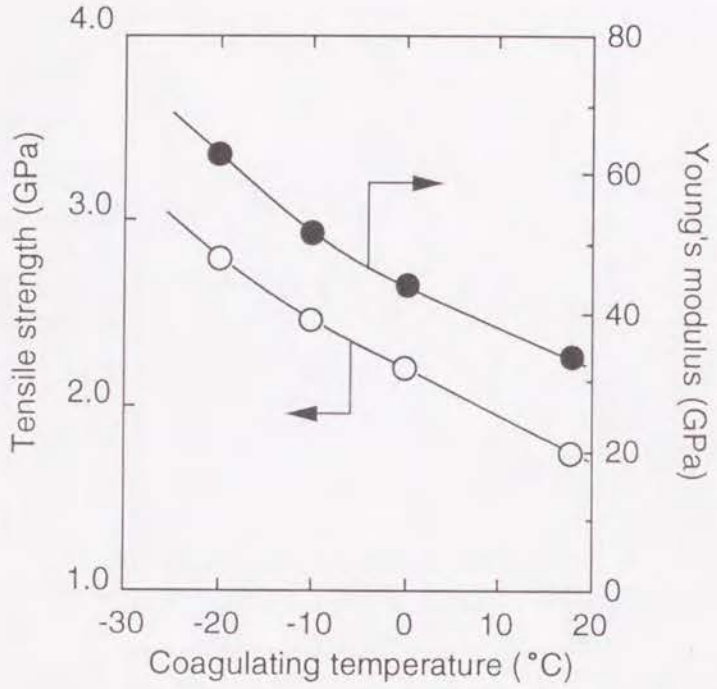

Figure 8. The tensile strength and Young's modulus of PVA fibers drawn to the highest draw ratio as a function of coagulating temperature.
(DP=5,000, PVA conc.= 6 wt%, and 80 wt% DMSO)

The tensile strength and Young's modulus of PVA fibers spun at various coagulating temperatures and subsequently drawn to the highest draw ratio are presented in Figure 8. The highest strength and Young's modulus obtained are 2.8 and 64 GPa, respectively. These fibers were spun at the lowest coagulating temperature(−20°C), followed by two-stage drawing at 160 and 200°C. It is again apparent that both the ultimate tensile strength and the Young's modulus decrease with rise in coagulating temperature.

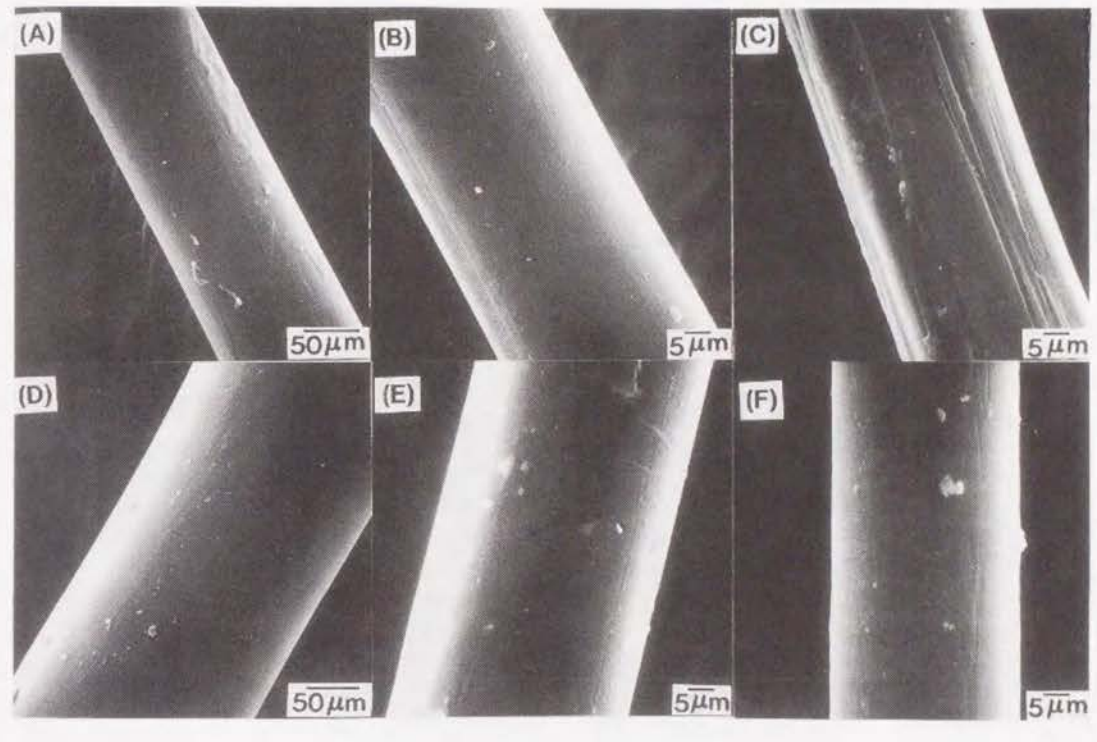

Figure 9. SEM photographs of the surface of PVA fibers spun from 6 wt% PVA dope of 80 wt% DMSO into methanol kept at different temperatures. (DP=5,000)
+18°C coagulation : (A) undrawn ; (B) x12 ; (C) x30
−20°C coagulation : (D) undrawn ; (E) x16 ; (F) x45

SEM microphotographs on the surface of PVA fibers drawn to different ratios are shown in Figure 9. It seen that the surface of PVA fibers before drawing was uniform in morphology. On the contrary, the surface of PVA fibers with the highest draw ratio was less homogeneous. Especially, the PVA fiber coagulated at +18°C and 30 times drawn exhibited a fibril texture.

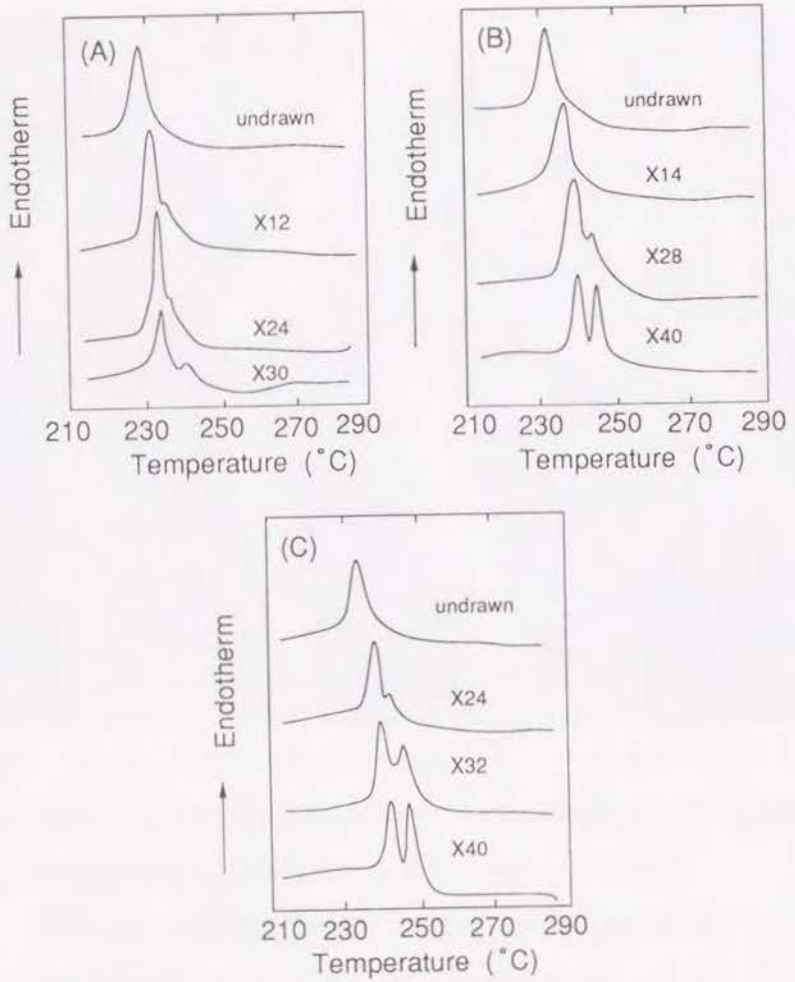

Figure 10. DSC thermograms of undrawn PVA fibers obtained by coagulation at different temperatures. (DP=5,000)
(A) +18°C ; (B) −10°C ; (C) −20°C

DSC curves of the above fibers are shown in Figure 10. It is interesting to note that two well−isolated peaks appear in the fusion curves along with the increasing melting temperature when the draw ratio of fiber becomes large.

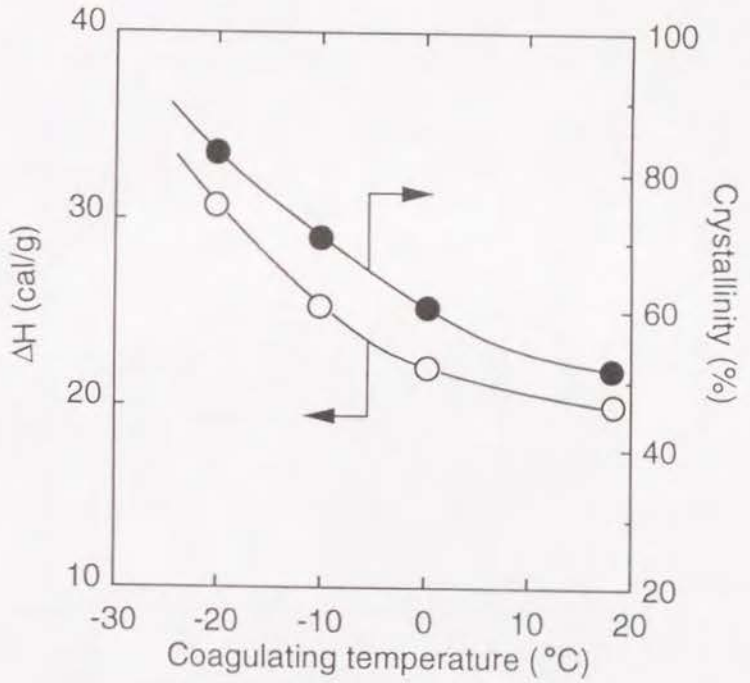

Figure 11. ΔH and crystallinity of PVA fibers drawn to the highest ratio as a function of coagulating temperature.
(DP=5,000, PVA conc.=6 wt%, and 80 wt% DMSO)

Figure 11 shows the dependence of ΔH and crystallinity of the most highly drawn PVA fibers on the coagulating temperature. Both the ΔH and crystallinity values were calculated from the thermogram area of DSC curves. The crystallinity of 45 times drawn PVA fiber was virtually identical to that calculated from the fiber density. The crystallinity of PVA fiber continuously increases as the coagulating temperature becomes lower, in other words, as the highest draw ratio increases. This is the same tendency as the strength and modulus.

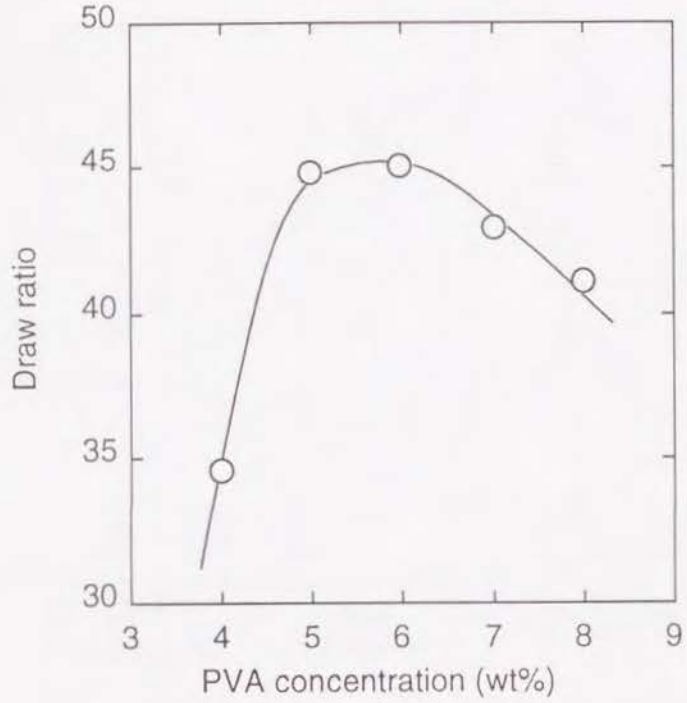

Figure 12. The highest draw ratio of PVA fibers coagulated in methanol at −20°C as a function of PVA concentration of spinning dope. (DP=5,000 and 80 wt% DMSO)

3. Effect of PVA concentration in dope

The highest draw ratio of PVA fibers coagulated at −20°C is shown in Figure 12 as a function of PVA concentration of the spinning dope. The dope was prepared from the H_2O/DMSO(20/80, w/w) solvent and the two-stage drawing was attempted. The highest draw ratio depends on the PVA concentration during spinning, giving the highest ratio at 6 wt%.

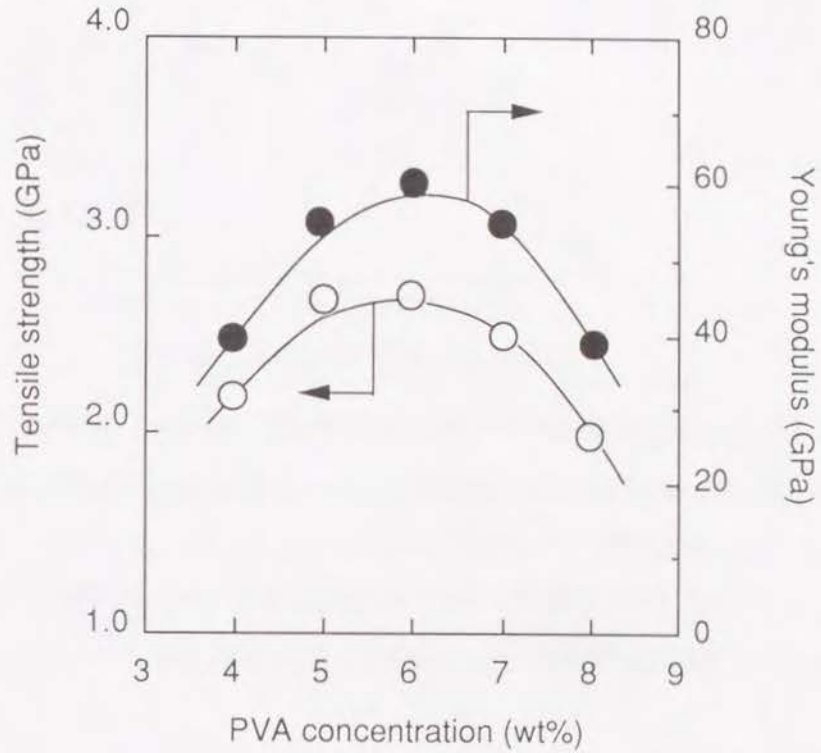

Figure 13. The tensile strength and Young's modulus of drawn PVA fibers coagulated in methanol at −20°C as a function of PVA concentration of spinning dope. (DP=5,000 and 80 wt% DMSO)

Figure 13 represents the effect of PVA concentration on tensile strength and Young's modulus of PVA fibers. As shown in Figure 13, the tensile strength as well as the Young's modulus of PVA fiber become maximum at the PVA concentration of 6 wt%, indicating the same tendency as for the highest draw ratio.

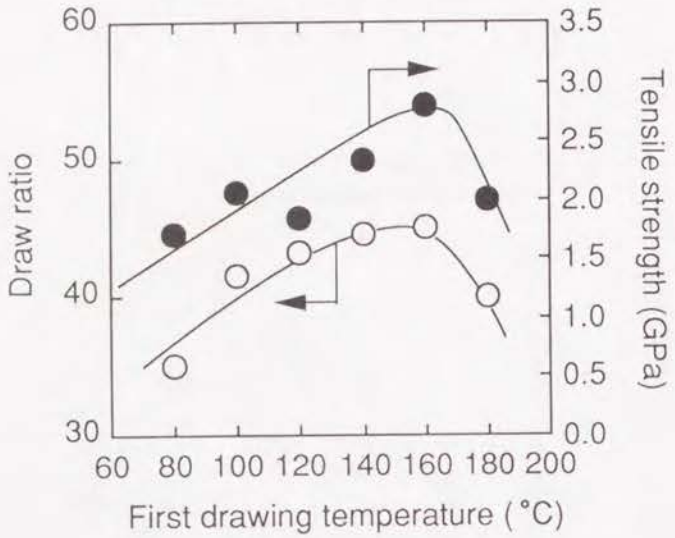

Figure 14. The highest draw ratio and tensile strength of PVA fibers coagulated in methanol at −20°C as a function of first drawing temperature.
(DP=5,000, 80 wt% DMSO, and second drawing temp.=200°C)

4. Effect of drawing temperature

As a preliminary experiment revealed that high draw ratio was not obtained by only one-stage drawing, two-stage drawing was applied in this study. Figure 14 represents the effect of first drawing temperature on the total draw ratio and the tensile strength of PVA fibers obtained at −20°C coagulating temperature, using 6 wt% PVA solution as spinning dope. The second drawing was carried out at 200°C. As can be seen in Figure 14, the total draw ratio increases up to 160°C and subsequently decreases. Further drawing at 200°C was difficult for the PVA fibers at temperature higher than 160°C and consequently the total draw ratio decreased when it was carried out at temperature higher than 160°C.

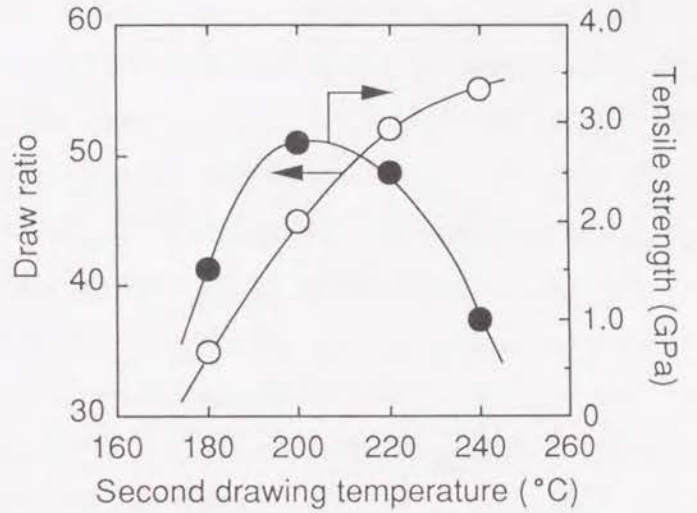

Figure 15. The highest draw ratio and tensile strength of PVA fibers coagulated in methanol at −20°C as a function of second drawing temperature.
(DP=5,000, 80 wt% DMSO, and first drawing temp.=160°C)

Furthermore, it is seen that the tensile strength becomes maximum at the first drawing temperature of 160°C. The effect of second drawing temperature on total draw ratio and the tensile strength of PVA fibers is shown in Figure 15. The first drawing was done at 160°C. The total draw ratio increases with the increasing second drawing temperature. However, the tensile strength increases up to 200°C and then decreases drastically. The PVA fiber became collared above 200°C, indicating extensive thermal degradation. As 240°C is close to the melting temperature of PVA fibers, slipping between the PVA chains may take place, making the drawing at higher second drawing temperature ineffective.

DISCUSSION

As described above, the PVA fiber obtained by gel spinning from the H_2O/DMSO(20/80, w/w) mixed solvent was found to have the highest draw ratio, resulting in formation of the highest strength and the highest Young's modulus fiber. Kanamoto et al. derived an equation relating the minimum draw ratio(DR_{min}) necessary for full chain extension of PVA molecular chain to DP, as given below[22]:

$$DR_{min}=0.41DP^{1/2} \qquad (2)$$

This equation gives about 30 times draw ratio as DR_{min} of PVA fiber when PVA has DP of 5,000. As demonstrated above, the highest draw ratio of PVA fiber obtained from the H_2O/DMSO(20/80, w/w) mixture was 45 times, which was larger than DR_{min}. It follows that drawing of the PVA fiber obtained from the H_2O/DMSO(20/80, w/w) mixture must have fully extended PVA chains, making it possible to approach the theoretical strength and modulus if eq.(2) is correct.

The dependence of the solvent and composition on drawability, tensile strength, and Young's modulus of PVA fiber is similar to that of PVA hydrogel. High drawability of the PVA fibers obtained from the H_2O/DMSO(20/80, w/w) mixture may be accounted for by the unique property of mixture of H_2O/DMSO. Water and DMSO molecules can associate to form a 1:1 molar complex at the H_2O/DMSO ratio of 20/80, producing a new solvent which quite differs from 100 wt% water and 100 wt% DMSO. The weight ratio of 20/80 for H_2O/DMSO corresponds to the molar ratio of 1/1. In principle, a very good solvent does not give

rise to gelation of PVA because of very high solvation, whereas a very poor solvent causes formation of large crystallites which may reduce the effective crosslink density, leading to formation of weak gel. It is likely that the H_2O/DMSO(20/80, w/w) mixture is more poor solvent than 100 wt% water and 100 wt% DMSO, but is a good solvent compared with the H_2O/DMSO(40/60, w/w) mixture. As a result, the H_2O/DMSO(20/80, w/w) mixture probably meet the requirement for optimal gelation.

In the case of PE, ultrahigh molecular weights are required to produce high strength and high modulus PE fiber. However, high strength and high modulus PVA fiber could be obtained from PVA with a relatively low molecular weight. PVA has hydroxyl groups, whereas PE does not have such polar groups. The gelation system was discussed by Hu et al., in connection with the change in intensities of the NMR spectra of hydroxyl groups of PVA[23]. We believe that the potential lateral interaction among PVA chains through the hydroxyl groups has lead to quicker gelation, making possible the gel spinning from PVA even if it has much lower molecular weights than nonpolar PE. Also, we attempted gel spinning of PVA with different molecular weights to study the dependence of molecular weight of PVA on the tensile strength. We found that gel spinning was very difficult if PVA had high molecular weights such as 387,000(DP=8,800). The draw ratio decreased with the increasing molecular weight and the increase in tensile strength was slight at molecular weights higher than 220,000(DP=5,000).

The tensile strength and the Young's modulus of PVA fiber strongly depend on gel spinning conditions. As is evident from Figure 8, the strongest PVA fiber was obtained by coagulating 6 wt% PVA dope

in methanol kept at the lowest temperature, followed by two-stage drawing(160 and 200°C) of the dried fiber. Gel spinning under this condition gave the highest drawability of dried PVA fiber, supporting the well-known fact that the higher the drawability, the higher the tensile strength and modulus. The strongest PVA fiber obtained in this study had 45 times as draw ratio, 2.8 GPa as tensile strength, and 64 GPa as Young's modulus.

The above findings may allow us to propose a hypothetical mechanism for gel spinning of PVA from the H_2O/DMSO(20/80, w/w) mixture on the basis of the gelation mechanism of PVA in mixture of H_2O/DMSO[24]. The physical gelation of PVA in mixtures of H_2O/DMSO must be closely related to the crystallization conditions, as the transparent PVA hydrogel with high water content and high strength could be obtained by crystallization at low temperatures. When crystallized at −20°C, the crystallites acting as physical crosslinks in the PVA gel seem to be small in size and numerous in number, producing an transparent and strong gel. When a homogeneous polymer dope obtained by complete dissolution of PVA in a mixture from H_2O/DMSO(20/80, w/w) at such a high temperature as 140°C, is cooled by immersion in methanol kept at a sufficiently low temperature such as −20°C, the PVA chains may quickly undergo mobility reduction, resulting in formation of small nuclei due to local chain entanglement through hydrogen bonding among the PVA segments. As a result, the solution may instantly set to a strong gel before macroscopic phase separation starts. The lower the coagulating temperature, the faster gelation would take place to produce stronger as-spun fibers. The macromolecular network having a relatively low entanglement density

will be fixed in this gel fiber and the removal of solvent from the gel fiber will not change this favorable intermolecular topology. Consequently, the PVA fiber coagulated at low temperatures may have a favorable entanglement density, resulting in formation of highly drawable PVA fiber. Formation of this weakly networked gel structure may allow the as-spun fiber to be drawn to a high ratio and hence high chain orientation along the fiber axis to yield high strength and high modulus fiber. On the contrary, when coagulating temperature is high, PVA solution may undergo macroscopic phase separation before gelation occurs because of insufficient formation of the three-dimensional network structure. Thus, spinning at high coagulating temperature may produce a heterogeneous PVA fiber, leading to low strength even after hot drawing. Since the freezing temperature of H_2O/DMSO(20/80, w/w) mixture is about −40°C, which is lower than that of 100 wt% water (0°C) and 100 wt% DMSO (18°C), the spinning dope prepared from the H_2O/DMSO(20/80, w/w) mixture can be coagulated at lower temperatures than that from 100 wt% water and 100 wt% DMSO, resulting in formation of more homogeneous PVA fiber.

The entanglement density of PVA fiber must be affected by the initial PVA concentration of spinning dope and be higher as the PVA concentration of spinning dope increases, resulting in formation of PVA fiber of lower drawability. On the contrary, if the dope concentration is too low, good PVA fiber cannot be obtained because of too low entanglement density. It is likely that the spinning dope prepared from PVA with DP of 5,000 and 6 wt% PVA concentration can produce the most favorable entanglement network between the PVA chains when deeply cooled.

The ultimate tensile properties of PVA fiber is affected also by drawing conditions. Indeed, the strongest PVA fiber could be obtained after two-stage drawing at 160 and 200°C in this study. It is well known that effective drawing can be performed for crystalline polymer at around α_c relaxation of the crystalline region. Grubb et al. reported that α_c relaxation of PVA crystalline region for a PVA film increased with the increasing draw ratio[25]. This means that α_c relaxation of PVA increased upon first drawing, shifting the optimum second drawing temperature to higher temperature.

A fusion curve having dual or multiple peaks has often been reported also for other polymers such as polyethylene[26-28], poly(ethylene terephthalate)[29], and nylon-66[30], together with abnormally high melting temperature, when the polymers are crystallized at very high pressure or under conditions giving rise to high molecular orientation. Also, extremely high melting temperature was reported for PVA by Yamaura et al[31]. and Monobe et al[32]. When PVA is crystallized from the aqueous solution under high degree of stirring, such a dual peak has not yet been recognized. Hyon et al. studied the structure and physico-chemical properties of PVA film when stretched at the amorphous state, followed by annealing[33]. It was found that the PVA film showed a dual fusion curve and a very high melting temperature. Thus, the dual fusion curve and the high melting temperature seem to be general characteristics of polymers crystallized under the condition that induces high molecular orientation, regardless of the polymer type. This dual peak strongly indicates the presence of dual structure or a very highly ordered crystalline phase of large dimension in addition to the normal crystalline region. Such a dual structure may be seen in the shish-kebab structure

which contains both the folded and the extended crystalline chain, as already confirmed for PE[34].

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SUMMARY

Chapter 1

PVA hydrogels with high strength and high water content were prepared by freezing the concentrated aqueous PVA solutions below their freezing points, followed by slow crystallization of frozen polymer above their freezing points. When a 30 wt% aqueous solution of PVA with the degree of polymerization of 1750 and the degree of saponification of 99.5 mol% was frozen at −20°C for 24 hr and then slowly thawed at 5°C for 10hr, a hydrogel was obtained, which exhibited the tensile strength of 60 kg/cm^2 and the elongation at break of 500%. The tensile strength and elongation became 35 kg/cm^2 and 400%, respectively, for a PVA gel prepared by thawing the frozen solution at 20°C for 3hr. X−ray and SEM studies revealed that the gels had a semi−crystalline and micro−porous structure.

Chapter 2

The transparent PVA hydrogels with high water content and high strength were prepared by low temperature crystallization of PVA solutions in mixed solvents consisting of water and a water−miscible organic solvent. The strength and transparency of PVA hydrogel were dependent on the type of organic solvent, the mixing ratio of water/organic solvent and crystallization temperature. A mixed solvent from water/dimethyl sulfoxide(DMSO) resulted in the highest

transparency and the highest tensile strength among the water/organic solvent combination studied at the lowest crystallization temperature. The tensile strength and the elongation of PVA hydrogel prepared from water/DMSO=20/80(w/w) were about 2 and 1.5 times as high as that of PVA hydrogel prepared from water alone. This result is related to the unique solvency of DMSO to PVA.

Chapter 3

PVA hydrogel with low water contents could be prepared by low temperature crystallization of PVA solution in water/DMSO mixtures, followed by high temperature annealing after drying and subsequent reswelling with water. The annealing resulted in an increase of crystallinity of PVA and also, unexpectedly, an increase of the water content of hydrogels when the degree of polymerization(DP) of PVA was 11,000. The tensile strength and dynamic modulus of PVA hydrogels increased with annealing, irrespective of DP of PVA, but always at the sacrifice of the water content of the hydrogel. In addition to the mechanical strength, the hardness and wear resistance of PVA hydrogels were improved by lowering the water content. The wear resistance of PVA hydrogels was greatly affected by DP of PVA when compared at a similar water content. The highest tensile strength(20MPa) and the highest dynamic modulus(180 MPa) were obtained when hydrogel was prepared from PVA with DP of 11,000 and annealed at 140°C for 24 hr. The water content of this hydrogel was 16 wt% and remained unchanged even if kept in water at 37°C for 85 days. The wear resistance of this hydrogel was higher than that of ultrahigh−

molecular-weight, high-density polyethylene.

Chapter 4

Low temperature gelation of PVA solution was performed in the presence of $CaCl_2$. The resulting PVA hydrogels showed high stickiness and excellent water-holding ability. These properties became more remarkable with the increasing $CaCl_2$ concentration in solvent. Furthermore, both the peel strength on stainless steel and the degree of swelling of the PVA hydrogel drastically increased as the $CaCl_2$ concentration increased from 20 to 30 wt%. It was concluded that the sticky and water-holding properties of PVA hydrogels were intimately related to the state of hydration of Ca ions in the aqueous environment.

Chapter 5

The physical state of water in PVA hydrogel was studied with the differential scanning calorimetry(DSC) to predict the microstructure of the PVA hydrogels. They were prepared with three different methods, including chemical crosslinking with glutaraldehyde, annealing of dried film, and crystallization at low temperature. The water in PVA hydrogels could be classified into three; free water, intermediate water, and bound water. The concentration of bound water was practically not dependent on the total water content of the hydrogels when prepared by low temperature crystallization or annealing of PVA film. The gel prepared by low temperature crystallization had less bound water than that by annealing of a cast film. Furthermore, the concentration of bound

water became higher as DP of PVA increased, whereas the reverse tendency was observed for the intermediate water. From these results it was concluded that the low temperature crystallization method gave a relatively larger free space between the PVA microcrystallites and the larger size of microcrystallites than the annealing method. It was also likely that PVA of higher DP provided a larger amount of free PVA chains which were not involved in microcrystallites.

Chapter 6

Translucent and transparent PVA hydrogels were prepared by low temperature crystallization technique from PVA solutions in water and a mixed solvent of water/DMSO(20/80, w/w). Protein adsorption was conducted at 37°C using ^{125}I-labeled γ-globulin(IgG), bovine serum albumin(BSA), and lysozyme. The behavior of protein adsorption on PVA hydrogel prepared by the low temperature crystallization technique was affected by the structure of PVA hydrogel and the type of protein. The amount of protein adsorbed on the transparent PVA hydrogel was much less than that on the translucent PVA hydrogel and poly(2-hydorxyethyl methacrylate)(PHEMA) hydrogel. The amounts of IgG and BSA adsorbed on transparent PVA hydrogel were independent of the water content of PVA hydrogel, in contrast to lysozyme which showed decreased adsorption with the water content of PVA hydrogel.

Chapter 7

A new type of soft contact lens was developed from the PVA

hydrogel prepared by the low temperature crystallization technique using a water/DMSO mixed solvent. The PVA contact lens material had a water content of 78 wt% and a tensile strength of 50 kg/cm^2, five times as strong as that of commercial PHEMA soft contact lens. The amount of proteins adsorbed to the PVA soft contact lens material was half to one thirtieth of that of the conventional soft contact lenses. Histological and scanning electron microscopic observation of rabbit eyes which had worn the PVA soft contact lens for 12 weeks showed no difference in corneal epithelium and cell arrangement in the corneal epithelium from wearing eyes.

Chapter 8

Gel spinning of PVA was attempted from the PVA dope prepared from the mixture of water and DMSO. The water/DMSO=20/80(w/w) mixture and methyl alcohol were found to be the best solvent for the spinning dope and coagulant, respectively. PVA fiber with the highest strength and Young's modulus were obtained from the undrawn gel fibers when subjected to hot two-stage drawing under conditions such as to produce maximum drawability. Furthermore, higher draw ratios of PVA fiber were attained for 6 wt% dope by lowering the coagulating temperature of methyl alcohol. In the present work, the highest tensile strength(2.8 GPa) and the highest Young's modulus(64 GPa) were realized, when the spinning dope was prepared from PVA with DP of 5,000 and water/DMSO(20/80, w/w) mixed solvent to have the PVA concentration of 6 wt%, the coagulating temperature of methyl alcohol was −20°C, and two-stage drawing was carried out at 160(first) and

200°C(second). The PVA fiber prepared under this gel spinning condition could be elongated to 45 times draw ratio. The very high drawability of PVA fibers obtained from the water/DMSO(20/80, w/w) mixture dope was ascribed to the ability of the water/DMSO mixture to promote gelation.

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Chapter 1.

1. Suong-Hyu Hyon, Won-Ill Cha, and Yoshito Ikada
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Chapter 7

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